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Part I. An investigation into the synthesis of allenes by the pyrolysis of homopropargylic alcohols. Part II. A study of the pyrolysis of the hydrogen and methyl phthalate esters of the cis- and trans-1,2-dimethylcyclohexanols.

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PART I

AN INVESTIGATION INTO THE SYNTHESIS OF ALLENES BY THE PYROLYSIS OF HOMOPROPARGYLIC ALCOHOLS

PART II

A STUDY OF THE PYROLYSIS OF THE HYDROGEN AND METHYL PHTHALATE ESTERS OF THE CIS- AND TRANS-1,2-DIMETHYLCYCLOHEXANOLS

By

HARRY H. HOLTON

A DISSERTATION

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To Mary Lou

ABSTRACT

PART I

The pyrolysis of homopropargylic alcohols has been proposed as a new synthetic route to allenes, and a model compound for the pyrolysis, 1,1,4-triphenylbutyn-1-ol, has been synthesized in 5% yield. Possible causes for the poor yield from the synthetic route chosen to prepare the alcohol are discussed.

The model compound has been pyrolyzed in the gas-liquid chromatographic instrument and the products of the pyrolysis have been recovered and partially identified. Only a small amount of the desired product phenylallene was formed, and possible reasons for the failure of the pyrolysis are discussed.

Pyrolysis of the model compound in the neat under an inert atmosphere and in solvents (nitrobenzene, N,N-dimethylformamide, and Diglyme) have failed to yield any identifiable products.

Suggestions for further research in this area are included.

PART II

The pyrolysis of cis- and trans-1,2-dimethylcyclohexyl hydrogen phthalate esters, both in the neat and in solvent,

has been studied.

The results of kinetic and product distribution studies on the neat pyrolysis of the corresponding methyl phthalate diesters are reported. The observed decrease in the rate of pyrolysis and the shift of the product distribution in the Hofmann direction are interpreted as evidence for acid proton participation in the rate controlling and product-determining steps of the neat pyrolysis of the hydrogen phthalate esters.

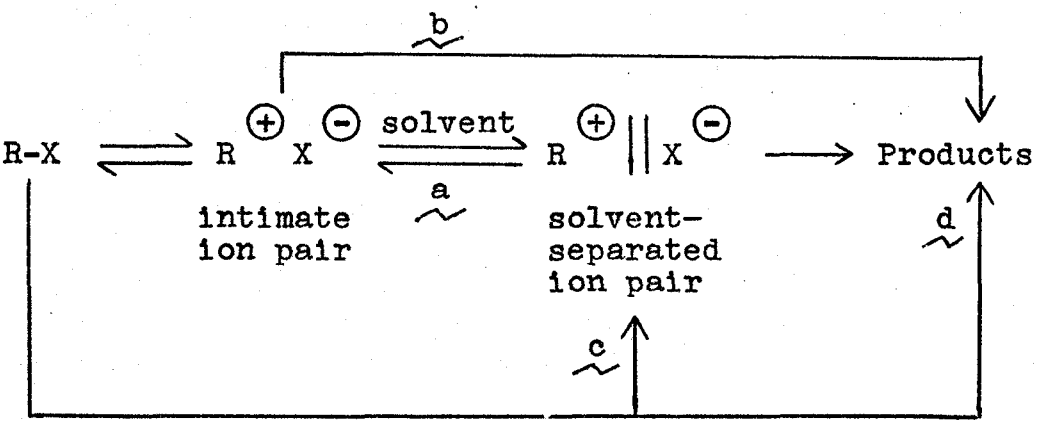
The results of kinetic studies, product distribution studies, isotope exchange studies and geometrical isomerization studies on the neat pyrolysis of cis- and trans-1,2-dimethylcyclohexyl hydrogen phthalate esters are reported. These results are consistent with a similar pyrolysis mechanism for both esters. This mechanism involves reversible formation of an intimate ion pair as the rate-determining step, followed by kinetically controlled elimination from the ion pair to produce products.

An identical series of studies on the pyrolysis of these same esters in solvent N,N-dimethylformamide (DMF) is also reported. The results of kinetic and product distribution studies on the pyrolysis of the methyl esters in solvent indicate that proton participation again occurs in the rate controlling and product-determining steps of the solution pyrolysis of the hydrogen phthalate esters.

The results of kinetic studies, product distribution studies, isotope exchange studies and geometrical isomer-

ization studies on the pyrolysis of the hydrogen phthalate esters in solvent are consistent with a similar pyrolysis mechanism for both esters. This mechanism involves the reversible formation of an intimate ion pair followed by an essentially irreversible formation of a solvent-separated ion pair as the rate-determining step. This in turn is followed by kinetically controlled elimination from the solvent-separated ion pair to produce olefins plus acid.

These results are used in conjunction with the results of similar studies on the pyrolysis of cis- and trans-1-phenyl-2-methylcyclohexyl hydrogen phthalate esters as the basis for the postulation of a general reaction scheme for pyrolytic eliminations.



The various pathways incorporated in this scheme can account for the behaviour observed in these systems and may be able to account for the behaviour observed in pyrolytic elimination reactions in general.

ACKNOWLEDGEMENTS

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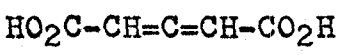
PART I

AN INVESTIGATION INTO THE SYNTHESIS OF ALLENES BY THE PYROLYSIS OF HOMOPROPARGYLIC ALCOHOLS

CHAPTER I

INTRODUCTION

The history of Allenes dates back to 1887 when Burton and Pechmann[1] unknowingly prepared glutinic acid (1) while attempting to prepare an acetylenic acid (2) (Figure 1). The first intentional synthesis of allenes was reported in 1888, but there was little



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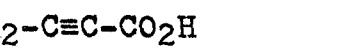

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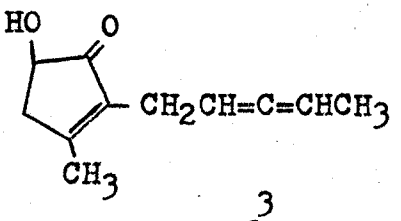
Figure 1 - Burton and Pechmann's Acids

further effort in this direction for several years, as most chemists felt that allenic type structures (and certainly cumulenes) would be unstable.[1] The isolation of a naturally occurring allene, pyrethrolone (3), was

first reported by Staudinger and Ruzicka in 1924.[1] Since their structural assignment was only tentative, some authors[2] give credit to Celmer and Solomons[3] for the first isolation of an authentic, naturally occurring allene, the antibiotic mycomycin (4), which is active against Gram-positive and Gram-negative bacteria including Mycobacterium Tuberculosis. Many more



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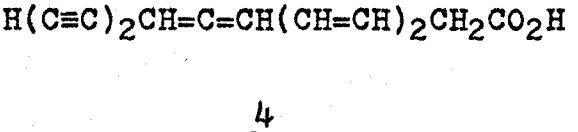

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Figure 2 - Pyrethrolone and Mycomycin

naturally occurring allenes have since been discovered,[1,2] and their not infrequent occurrence in nature provides ample cause for interest in their synthesis.

The reactions of allenes as synthetic intermediates provide further cause for interest in their preparation. The double bonds of their unique cumulated system may be reacted either singly or in conjunction with one another[4] to produce many products difficult to obtain by routes not involving allenes. Although mixtures are sometimes obtained, the major product is often both predictable and controllable by variation of both the substitution on the allene and the nature of the attacking group.[2,4] Thus, electrophilic radicals usually attack the terminal

carbon atom, while nucleophilic radicals will usually attack the central carbon atom. Similarly, nucleophilic ionic attack occurs primarily on the central carbon atom due to its sp hybridization and the products are fairly predictable since Markownikoff's rule is generally followed.[2]

Allenes may be either fully- or semi-hydrogenated.[4] The latter is particularly facile in the case of cyclic allenes.[5]

Carbenes readily add to allenes to produce alkylidene-cyclopropanes,[6,7] and cyclopropenones may be prepared by hydrolysis of the cyclopropenyl chlorides formed by the action of dichlorocarbene on allenes (Figure 3).[8]

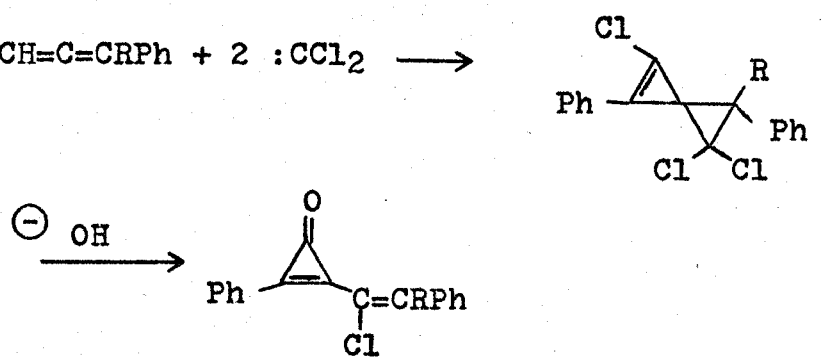


Figure 3 - Preparation of Cyclopropenones From Allenes

Ketones are the major products resulting from the hydroboration of allenes, and as allenes are more reactive than olefins, they may be selectively reacted in the presence of olefins (Figure 4).[9]

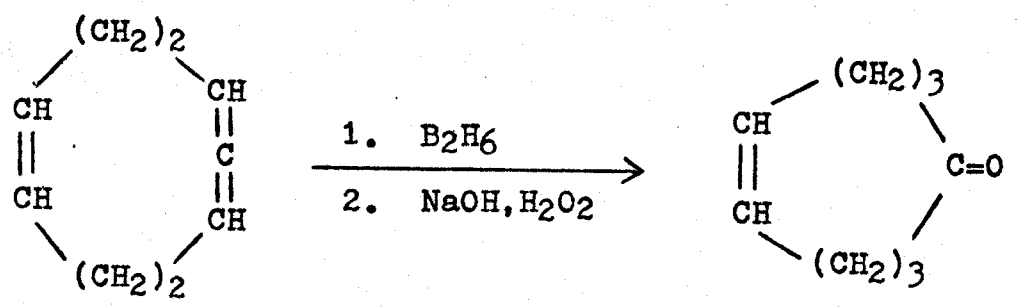


Figure 4 - Selective Hydroboration of Allenes in the Presence of Olefins

The action of silver oxide in water on β -allenic halides constitutes a general synthetic route to cyclopropyl ketones (Figure 5).[10]

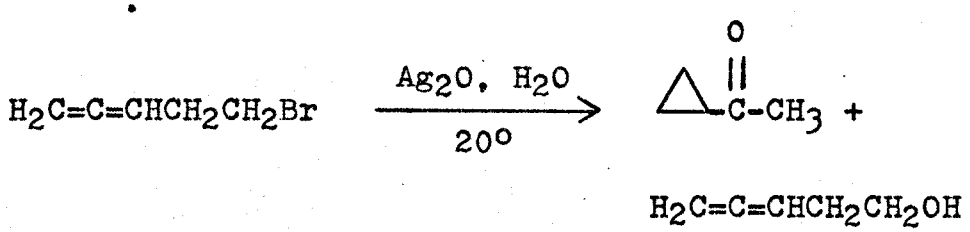


Figure 5 - Rearrangement of β -Allenic Halides to Cyclopropyl Ketones

Although the Diels Alder reaction with allenes has not been studied to a great degree, allenes are good dienophiles and good yields usually result.[11] Furthermore, allenes may be used as dienes in this reaction when there is an α,β -unsaturation present, as in vinylallenes (Figure 6).[12]

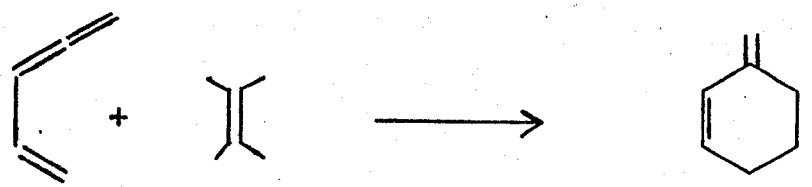


Figure 6 - Diels Alder Reaction of Vinylallenes With Olefins

Allenes may be dimerized,[13] trimerized, tetramerized, and polymerized.[2,4,14,15] The list of allene reactions is long, and their synthetic utility and versatility is well recognized.[2,4] Thus, it is not surprising that there appears to be almost as many synthetic routes to allenes as there are "known" allenes.

The great abundance of specific methods for the preparation of allenes may perhaps be a result of the fact that there is a relative lack of general routes to allenes. Out of more than sixty specific methods which are broken down into eight general reaction type classifications, Rutledge feels that there is only one method which deserves to be called a "general synthetic route" to allenes.[16] This route, (developed by Doering and LaFlamme),[17] comes under the general classification of an elimination reaction and involves the dehalogenation of gem-dihalocyclopropanes. The addition of dichloro-

or dibromocarbene across the double bond of an olefin yields 1,1-dihalocyclopropanes,[18] which may be converted to allenes simply by treatment with metals (M) or metal alkyls (RM), often in excellent yield (Figure 7).[19]

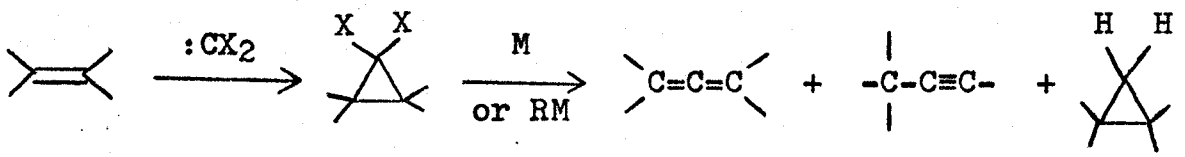


Figure 7 - Synthesis of Allenes by the Dehalogenation of gem-Dihalocyclopropanes

The commercial availability of many olefins and the relative absence of side reactions make this an exceptionally versatile route to allenes. There are, however, some problems. As in all synthetic transformations, the substrate must be inert to the reaction conditions (apart from the reactive site). The conditions under which the carbene is generated and the dehalogenation effected are usually quite basic, and this may be a limitation in terms of what substrates may be used. A more important problem is the fact that allenes are not the exclusive products of this reaction. Acetylenes[17,20] and alkylcyclopropanes,[4] are known to be formed also, and these side products are

often difficult to separate from the desired allene.

Besides the dehalogenation of gem-dihalocyclopropanes, Taylor[2] feels that the reaction which involves a 1,4 addition to vinylacetylenes represents the one other route to allenes that is noteworthy (Figure 8).

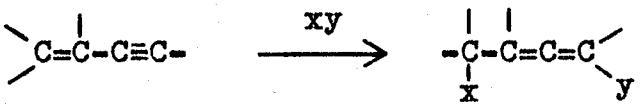


Figure 8 - Synthesis of Allenes by 1,4 Addition to Vinylacetylenes

This is a most versatile route, since a variety of "xy reagents" may be used. In particular, if xy is a lithium alkyl (RLi), then the anion formed by its 1,4 addition to the vinylacetylene may be reacted further in many ways to produce a wide range of functionally substituted allenes which include alcohols, acids, amides, ketones, and others.[2]

The weakness of this method lies in the fact that, again, allenes are not the exclusive products. If 1,2 or 3,4 addition takes place (Figure 9), then acetylenes or 1,3-dienes result and thus mixtures frequently occur in this reaction. These side products are again difficult to separate from the desired allene. This problem may be partially circumvented by a careful match of the xy reagent

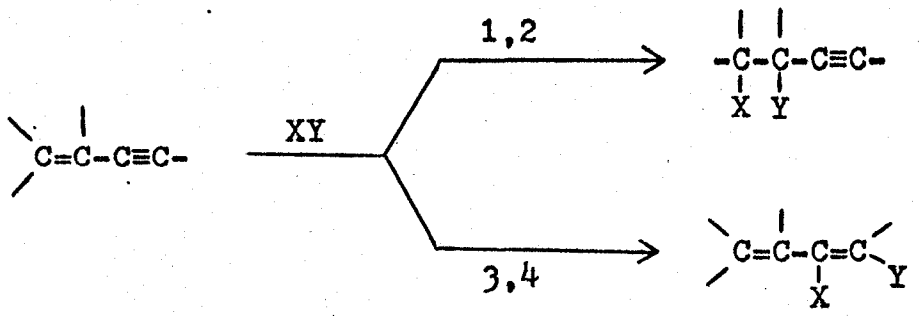


Figure 9 - 1,2 and 3,4 Additions to Vinylacetylenes

with the particular vinylacetylene so that a maximum amount of the 1,4 addition product is obtained. These requirements impose limitations on the versatility of this method, and even under the best of conditions, some substituted acetylene or diene is likely to be formed.

Of the many other methods known for the synthesis of allenes, none is considered as satisfactory as either of the two methods discussed above.[2] Both of these methods have shortcomings in terms of reaction conditions and side products which are difficult to remove. Thus there is definitely room for improvement as regards the search for general synthetic routes to allenes.

Almost all of the known routes to allenes appear to suffer from either or both of two common problems. Either the synthetic route is nonspecific and produces side products, or the allene produced is unstable under the reaction conditions used to generate it. The first problem is usually encountered when more than one reaction

mechanism or more than one point of reagent attack is possible.[2] The second problem is frequently encountered when the reaction conditions used to generate the allene are basic. It is a well-known fact that allenes isomerize to mono-substituted acetylenes, di-substituted acetylenes, or conjugated dienes under basic conditions.[4]

An idealized synthetic route would eliminate both of these problems. The reaction conditions would be non-basic, and the reaction mechanism would allow for only one product. A synthetic route which could conceivably meet these requirements might be the pyrolysis of homo-propargylic alcohols in which it is plausible that only one reaction mechanism would be followed, and the reaction conditions would remain neutral (Figure 10). The proposed

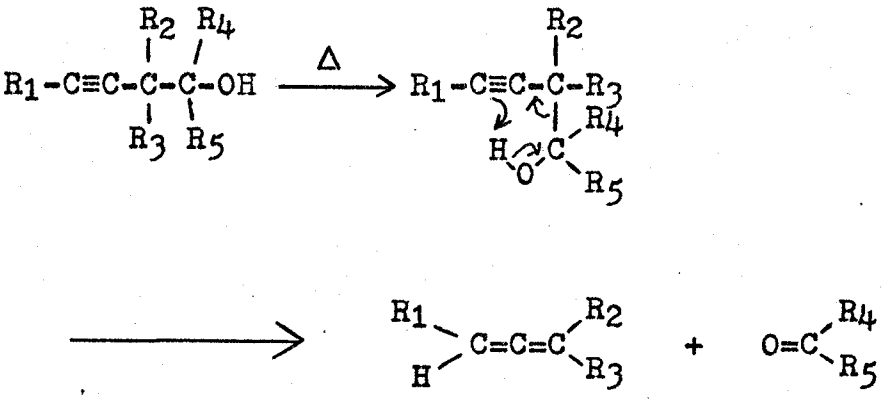


Figure 10 - Proposed Synthesis of Allenes by the Pyrolysis of Homopropargylic Alcohols

mechanism for the combination propargylic rearrangement-elimination should lead exclusively to the allene with the formation of no acetylenes or dienes. The other elimination product (the ketone) is neutral and should not catalyze isomerization of the allene. This type of reaction is not without precedent, as the pyrolysis of propargyl vinyl ethers (a Claisen-type rearrangement) is known to lead to allenic aldehydes in up to 90% yield, often at low (120-150°) temperatures (Figure 11).[21]

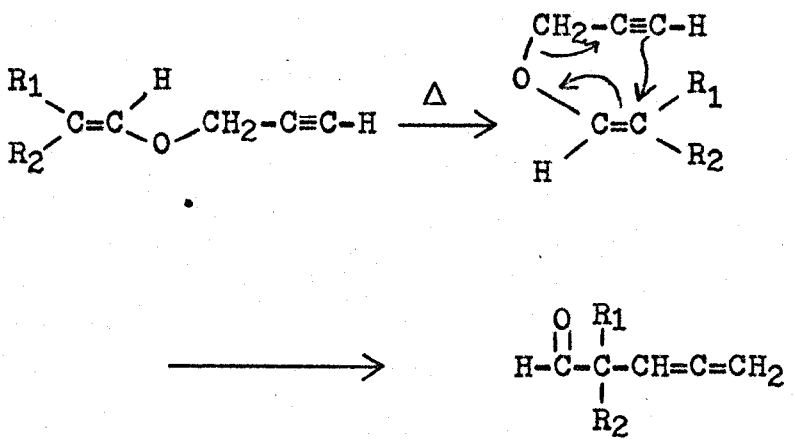


Figure 11 - Pyrolysis of Propargyl Vinyl Ethers

Similarly, the pyrolysis of dipropargyl acetals also gives allenic aldehydes,[22] and the Cope rearrangement of isobutenylpropargyl malonate gives the allenic diester (Figure 12).[23]

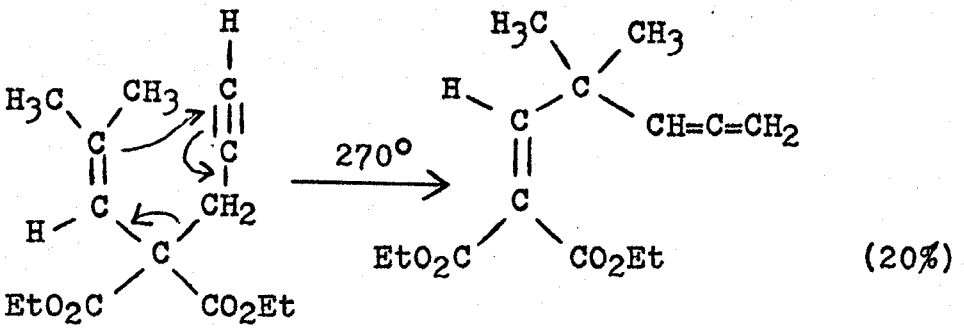


Figure 12 - Cope Rearrangement of Isobutenylpropargyl Malonate

Thus, the cyclic mechanism proposed for the pyrolysis of homopropargylic alcohols is not unreasonable and the pyrolysis of alcohols of this type could provide a general synthetic route to allenes uncontaminated with side products. Therefore, a study of a specific example of such a pyrolysis was undertaken in order to determine the feasibility of the proposed synthetic route to allenes.

CHAPTER II

RESULTS AND DISCUSSION

The Choice and Synthesis of the Model Compound 1,1,4-Triphenylbutyn-1-ol

The proposed synthetic route to allenes involves the pyrolysis of homopropargylic alcohols as shown in Figure 10. For the test pyrolysis, it was decided that R_2 and R_3 should be hydrogens as it was expected that this would simplify both the synthesis of the alcohol and the identification of the pyrolysis products. Similarly, it was decided that R_1, R_4 and R_5 would be phenyls as both starting materials and products would be known, readily available materials. Thus, the model compound chosen to be pyrolyzed was 1,1,4-triphenylbutyn-1-ol (10), and the expected pyrolysis products are phenylallene (13) and benzophenone (21).

The synthetic route chosen for the preparation of the model compound is shown in Figure 13.

The conversion of phenylacetylene (5) to the corresponding Grignard reagent (6) was accomplished by the exchange reaction with ethylmagnesium bromide. The reagent was reacted *in situ* with formaldehyde gas and yielded phenylpropargyl alcohol (7) after hydrolysis. The alcohol (7) was converted to phenylpropargyl

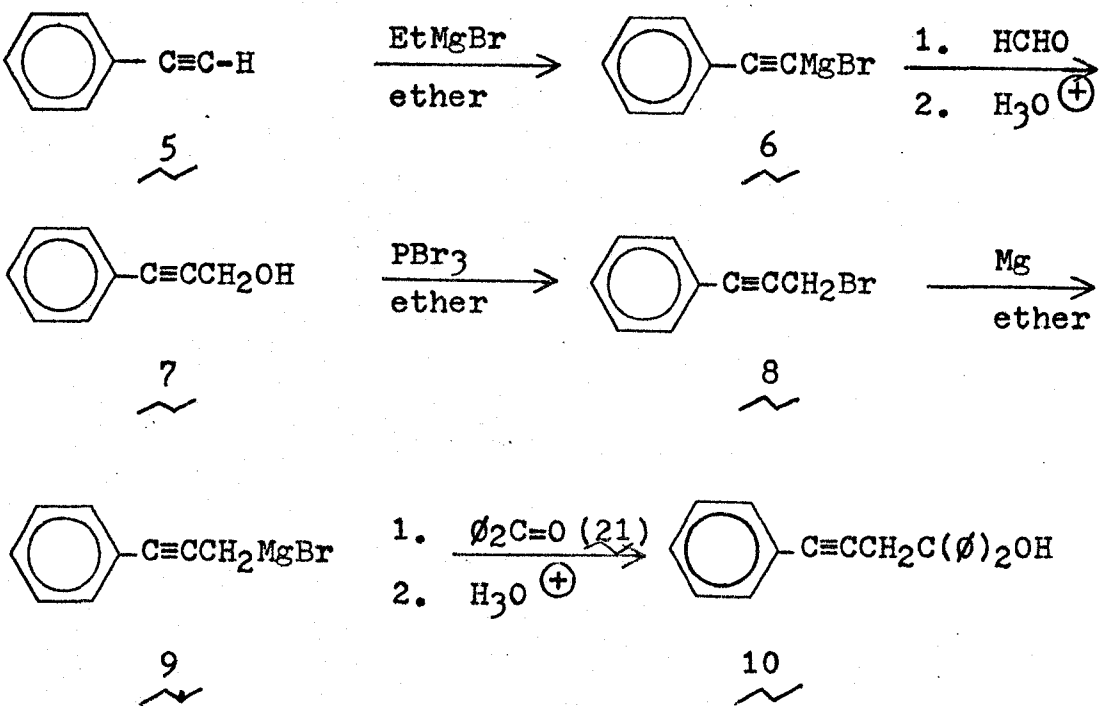
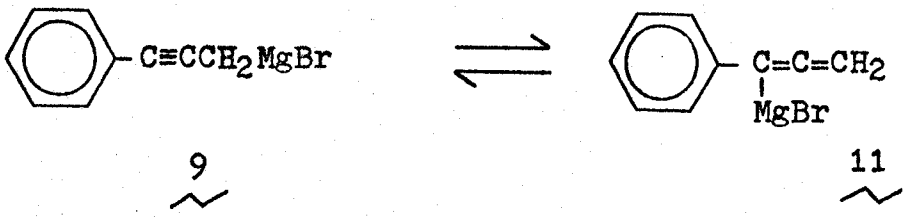


Figure 13 - Proposed Synthetic Route for the Preparation of 1,1,4-Triphenylbutyn-1-ol

bromide (8) by the action of phosphorous tribromide and the bromide was subsequently converted to the Grignard reagent (9) with magnesium in ether. The reaction of 9 with benzophenone (21) produced 1,1,4-triphenylbutyn-1-ol (10) in nine per cent yield. All attempts to improve the yield of this last step by the use of longer reaction times and more vigorous reaction conditions failed. The cause of the apparent incomplete reaction is not known, but there are some possible explanations. Initial attack of the reagent (9) may be hindered by tautomerism of the

reagent as shown in Figure 14.[2,24] The allenic Grignard



9 11

Figure 14 - Tautomerism of the Phenylpropargyl Grignard Reagent

reagent produced (11) might well be a poorer nucleophile than 9, and thus decrease the rate of reaction. Indeed, it is well-known that such tautomerism frequently does occur with propargylic Grignard reagents and that no products from the attack of allenic Grignard reagents on ketones are observed.[2] These suggestions have been tested for this system by the preparation of 9 and the reaction of it with water (Figure 15). Both phenylmethylacetylene (12) and phenylallene (13) were formed in approximately equal amounts, indicating that the postulated tautomerism of 9 to 11 was in fact occurring. Furthermore, in the reaction of 9 with ketone, none of the alcohol which would result from attack of 11 on ketone was found.

Another possible cause of the poor yield from this reaction may be that the formation of the adduct of 9 with the ketone (21) is a reversible process, such as has been observed for the Crotyl system.[25] The adduct (14) formed

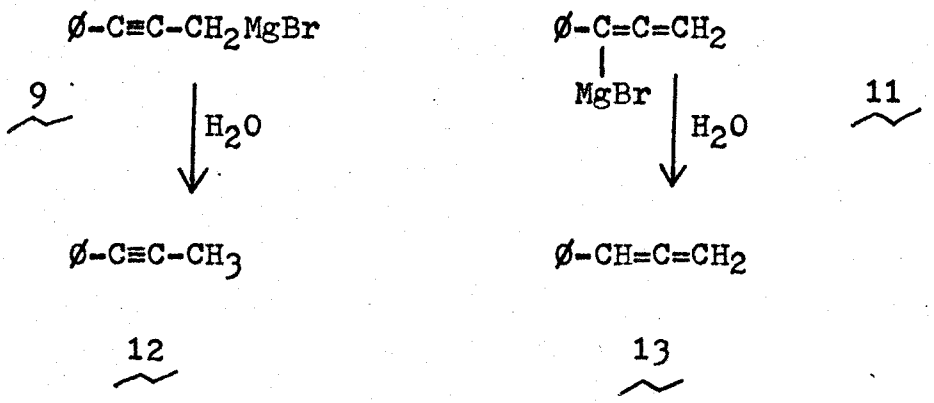


Figure 15 - Reaction of Phenylpropargyl Magnesium Bromide with Water

by attack of crotyl Grignard reagent decomposed to produce a new Grignard reagent (15) which then reattacked ketone to produce a new adduct (16) (Figure 16).

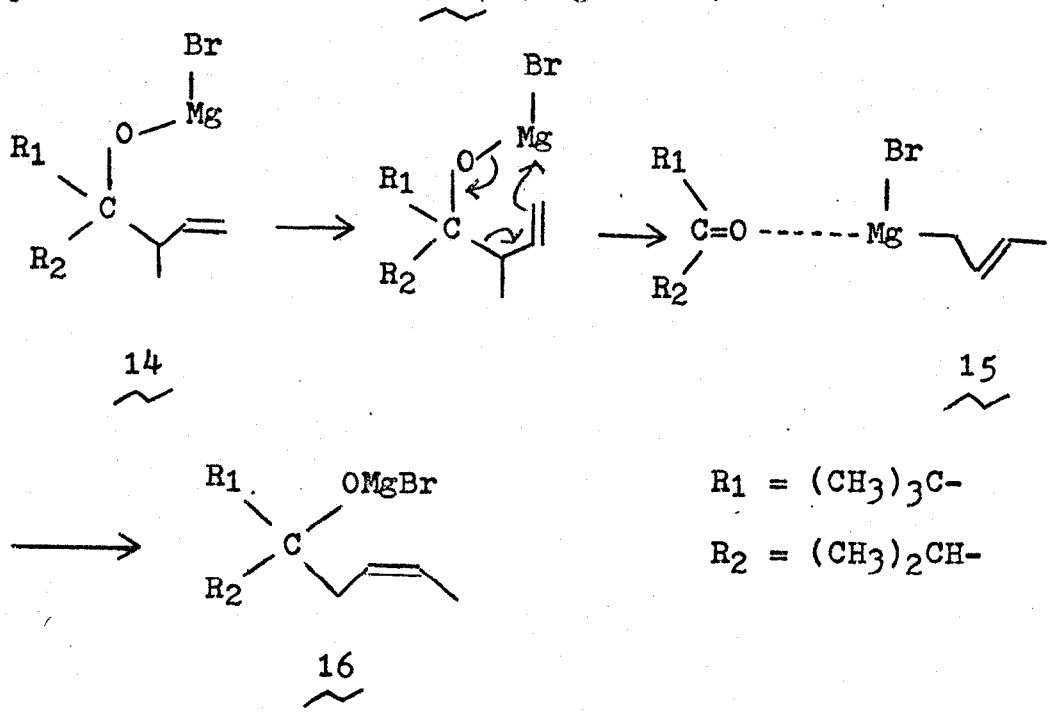


Figure 16 - Rearrangement of Grignard Adducts of Crotyl Magnesium Bromide

It is interesting to note that in the crotyl system, the amount of unreacted ketone left in the reaction actually increased with time. In the reaction of 9 with benzophenone a large amount of ketone does not react regardless of reaction time, conditions or relative concentrations. Thus in a manner analogous to the crotyl system, a reversible attack of propargyl Grignard reagent (9) on ketone may be occurring as is shown in Figure 17.

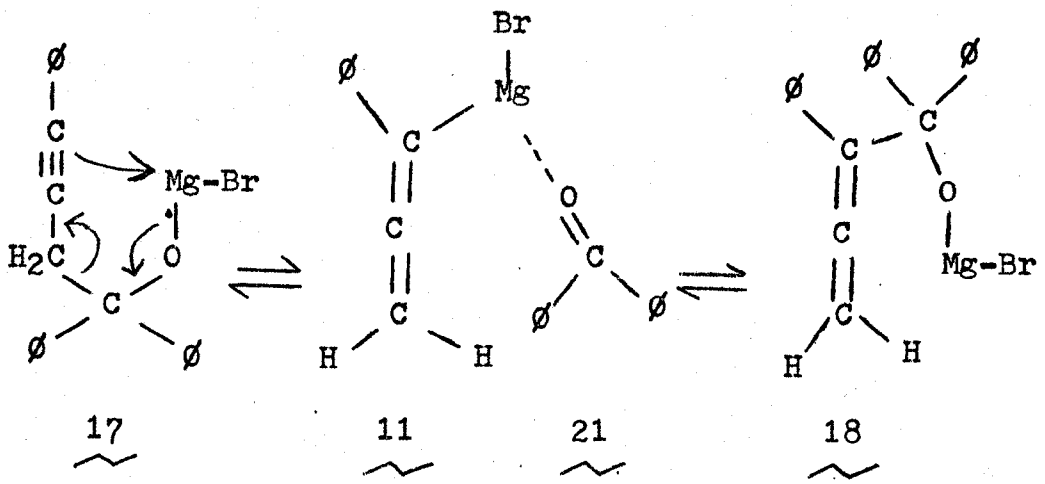


Figure 17 - Possible Reversible Decomposition of Phenylpropargyl Grignard Adduct

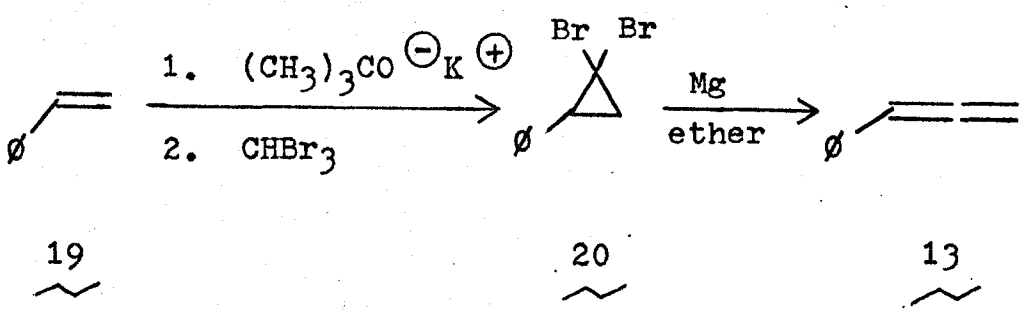
The adduct (18) which would result from attack of the allenic Grignard reagent on the ketone would also be subject to such a decomposition to reform Grignard reagent (9) plus ketone. A combination of these problems whereby propargylic Grignard reagent (9) tautomerizes to form allenic Grignard reagent (11) which will not attack

ketone, and whereby the adduct formed (17) from attack of 9 on ketone decomposes to form 11 plus ketone, could result in a very low yield of the desired product (10). In any event, the very low yield of the desired alcohol (10) indicates that this particular synthetic route to 10 is poor. Alternate synthetic routes such as the reaction of sodium-phenylacetylide with 1,1-diphenylethylene oxide may readily be envisaged.

Synthesis of Authentic Phenylallene

Authentic phenylallene was necessary for the purpose of comparison with pyrolysis products. The reaction sequence chosen to prepare phenylallene is as shown in Figure 7.

Attempts to synthesize phenylallene by the action of n-butyl lithium on 1,1-dichloro-2-phenylcyclopropane[26] failed to yield usable quantities of phenylallene. The major product appeared to be the corresponding terminal acetylene (benzylacetylene). The allene was successfully produced by the sequence shown in Figure 18. 1,1-Dibromo-2-phenylcyclopropane (20) was prepared by the action of dibromocarbene on styrene (19).[27] The reaction of magnesium metal with the gem-dihalide (20) generated phenylallene (13) in good yield.[17]



19 20 13

Figure 18 - Synthesis of Authentic Phenylallene

Pyrolysis of 1,1,4-Triphenylbutn-1-ol

A Pyrolysis in the Gas Chromatograph Instrument

Pyrolysis of 10 was first attempted in the gas chromatograph instrument (glc) with the hope that pyrolysis would occur in the injection port and would produce detectable products. A solution of 10 in chloroform was injected into the glc under standard conditions and using a variety of columns, temperatures and flow rates. The five peaks produced were analyzed by comparison of their retention times with those of authentic samples, and by infra-red (ir) and nuclear magnetic resonance (nmr) spectroscopy of the glc eluates (Figure 19). The first and third components to elute were the expected products phenylallene (13) and benzophenone (21). The second component

appeared to be 1,1,4-triphenylbutyene (22). The fifth component (23) was produced in too small an amount and was too contaminated with 22 to be identified. The allene (13) and the acetylene (12) were in a 30:70 ratio, and it was shown that 13 would not isomerize to 12 under the pyrolytic conditions by injection, collection and reinjection of authentic 12 and 13.

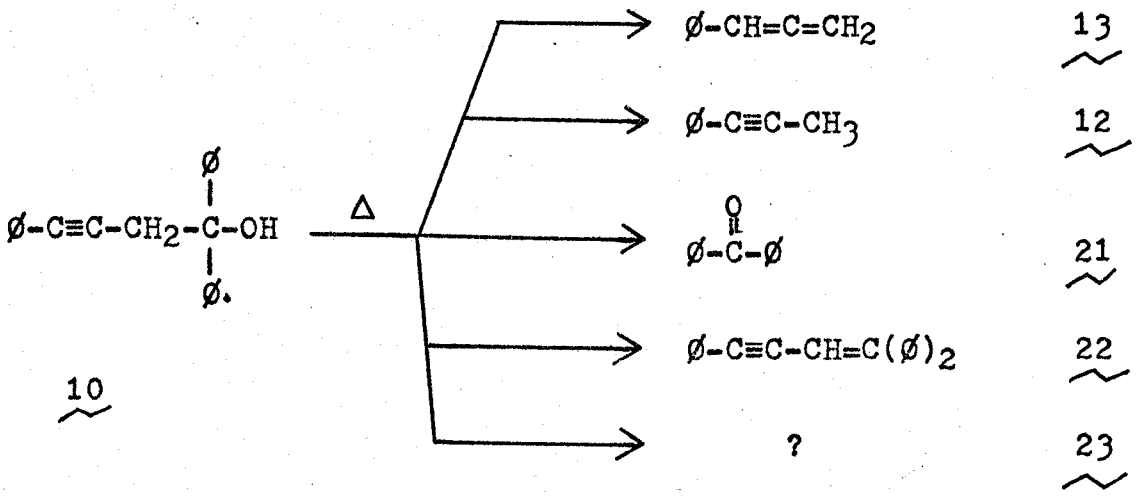
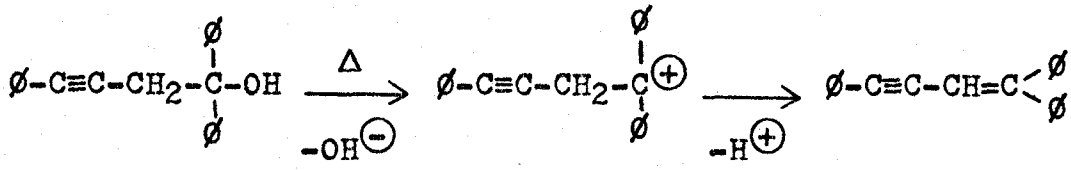


Figure 19 - Products From the Pyrolysis of 1,1,4-Triphenylbutyn-1-ol in the Gas Chromatograph

Thus, when pyrolyzed in the glc, the major amount of 10 merely dehydrated to produce 22. The remainder of 10 (that pyrolyzed) did not produce pure phenylallene, but instead produced a mixture of allene (13) and acetylene (12) of which 12 was in the major amount. In conclusion, the results of this study of the pyrolysis of 10 in the glc indicate that this route may be a failure as a synthesis of pure allenes.

The reason for the failure of the pyrolysis to yield pure phenylallene may lie in the mechanistic plurality of the decomposition of 10. A decomposition involving a six-membered cyclic transition state cannot account for all the pyrolysis products obtained, whereas a mixture of mechanisms can. Loss of hydroxide followed by subsequent loss of a proton would account for the formation of 22 (Figure 20).



10 22

Figure 20 - Possible Route for the Production of 1,1,4-Triphenylbutyene

It should be noted that the above process (Figure 20) is depicted in its crudest form. Loss of water may also occur from a kinetically controlled deprotonation of an ion pair produced by heating 10.

The formation of the other pyrolysis products 12, 13, and 21 may be explained by a mechanism which involves heterolytic (or homolytic) cleavage of the propargyl-carbinol bond (Figure 21).

A combination of the two mechanistic pathways depicted in Figures 20 and 21 could account for all the known

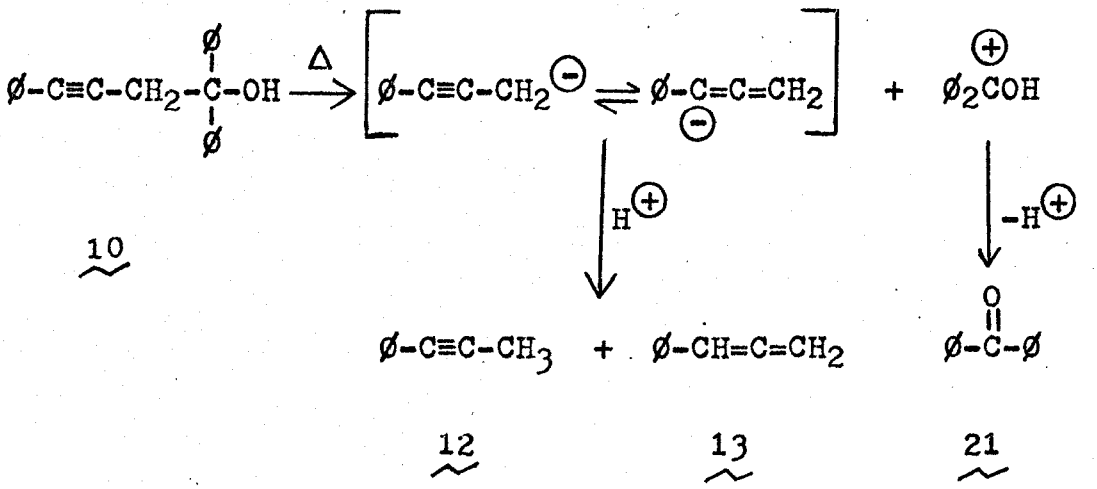


Figure 21 - Possible Heterolytic Mechanism for the Formation of Phenylallene and Phenylmethylacetylene

pyrolysis products. In any case, no matter what the mechanistic cause, the pyrolysis of 10 in the glc results in a very poor yield of phenylallene, and the allene is contaminated with an acetylene.

B Pyrolysis as a Neat Melt

1,1,4-Triphenylbutyn-1-ol was pyrolyzed as a neat melt in order to determine if a better yield of phenylallene (than was obtained from pyrolysis in the glc) would result. The alcohol (10) was pyrolyzed under an inert atmosphere at temperatures of 225°, 230°, and 250° for varying lengths of time. Volatile product was recovered by use of a cold trap and shown by ir analysis to be only benzophenone in all cases. Similarly, in all cases the

nonvolatile residue was found to consist mainly of starting material, plus benzophenone and an unidentifiable chromophore. Although benzophenone was generated, no phenylallene was detected. This may have been due to further reaction of the allene, perhaps dimerization or polymerization, both of which are known to occur when allenes are strongly heated.[2] In any event, phenylallene was not isolated, and it would appear that this method is unsuitable for the preparation of allenes.

C Pyrolysis in Solvents

It was felt that recovery of phenylallene might be feasible if pyrolysis were carried out in solvent. Furthermore, electrophilic trapping agents could be added in an attempt to trap any carbanionic species that might be generated in the pyrolysis (such as are pictured in Figure 21). Therefore, pyrolysis was carried out in nitrobenzene, N,N-dimethylformamide (DMF), and Diglyme. In each case, the reflux temperature of the solvent was employed and a period of 24 hr was used for the pyrolysis. No trapping agent was used for the pyrolysis in nitrobenzene, while 4-bromonitrobenzene was used in DMF and picryl chloride was used in Diglyme. In all of the pyrolyses neither phenylallene nor any carbanionic reaction products were detected. Pyrolysis in nitrobenzene and Diglyme yielded almost exclusively starting material. Pyrolysis in DMF led to

complete decomposition of starting material, but only small amounts of unidentifiable products were obtained.

SUMMARY AND CONCLUSIONS

1,1,4-Triphenylbutyn-1-ol has been synthesized and its pyrolysis has been studied in the glc, in the neat, and in solvents. Only in the case of pyrolysis in the glc were products separable and identifiable, and it was found that only a minor amount of the desired product phenyallene was formed. A great deal of further work is obviously required before any firm conclusions about the usefulness of this route to allenes may be drawn. However, the results of these test pyrolyses of this one model compound do indicate that the usefulness and scope of this route to allenes may be limited.

SUGGESTIONS FOR FURTHER RESEARCH

The further work suggested above should include the pyrolysis of other homopropargylic alcohols in order to determine the effects of structural changes on the pyrolysis. Also, further work on the pyrolysis of 10 at higher temperatures and under reduced pressure using a short contact time flow system should be carried out to determine if conditions conducive to the formation of the allene may be realized.

CHAPTER III

EXPERIMENTAL

Infra-red spectra were obtained using Beckman IR-10 and IR-12 spectrophotometers equipped with potassium bromide cells. All solutions were approximately 10 weight-weight per cent in the solvent specified. Absorptions are recorded in reciprocal centimeters (cm^{-1}) and only the significant absorptions are recorded. The intensities are expressed as weak (w, 100-75% transmission), medium (m, 74-40% transmission) or strong (s, 39-0% transmission). All nuclear magnetic resonance spectra were obtained using Jeolco C-60 and C-60HL instruments, and the chemical shifts are expressed in τ units downfield from internal tetramethylsilane. The splitting pattern of each resonance is reported using the following code: s = singlet, d = doublet, t = triplet, and m = multiplet. All solutions were weight-volume per cent in the solvent specified. All melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. All gas-liquid chromatography (glc) was performed on an F&M model 720 gas chromatograph under the following conditions: injector - 300°, detector - 300°, bridge - 100 mA, helium flow - 1 cc/sec and oven temperature as specified. The columns used are listed below.

TABLE I

COLUMNS USED FOR GAS-LIQUID CHROMATOGRAPHY

Column	Length (Ft)	Diameter (In)	Substrate
a	6	1/4	10% SE 30
b	8	1/4	20% SE 30
c	10	1/4	10% DEGS
d	8	3/8	10% SE 30
e	8	1/2	10% SE 30
f	8	1/2	10% PEG 20M

Peak areas were determined with a disc integrator.

Unless otherwise specified, all reactions were carried out in flame dried flasks using an inert atmosphere (N_2). All solutions were dried by the use of anhydrous magnesium sulfate. All solutions were concentrated in vacuo. All distillations were carried out using a vacuum jacketed 10 cm Vigreux column. All temperatures are recorded in degrees Centigrade and all pressures are recorded in millimeters of mercury.

Synthesis of 1,1,4-Triphenylbutyn-1-ol

1,1,4-Triphenylbutyn-1-ol (10) was synthesized according to the scheme shown in Figure 13.

A Phenylpropargyl Alcohol (7)

Magnesium turnings (7.5 g, 0.30 mole) were covered with 150 ml anhydrous ether in a one litre, three-necked Morton flask fitted with a high torque mechanical stirrer, a reflux condenser (drying tube attached) and an addition funnel. A solution of ethyl bromide (27.2 g, 0.30 mole) in 180 ml anhydrous ether was added dropwise at a rate sufficient to maintain a gentle reflux. After the addition was complete, the mixture was refluxed 30 min and cooled to room temperature. A solution of phenylacetylene (25.0 g, 0.25 mole) in 75 ml anhydrous ether was then added dropwise with vigorous stirring. After the addition was complete, the mixture was stirred 36 hr at 25°. Formaldehyde gas, generated by the pyrolysis of paraformaldehyde (18.0 g, 0.60 mole),[28] was forced into the solution with a stream of nitrogen. The semi-solid green mass that resulted was stirred at reflux temperature for 2 hr, cooled to 0° and washed three times with 200 ml portions of anhydrous ether. The solid mass was hydrolyzed with saturated, aqueous ammonium chloride and the two layers were separated. The aqueous layer was extracted twice with 100 ml portions of ether and the combined organic layers were washed twice with 100 ml portions of saturated, aqueous sodium chloride. The ethereal extract was dried, concentrated and distilled yielding 22.2 g (69%) of phenylpropargyl alcohol (7): bp 98-100° (1.0 mm); n_D^{25} 1.5835 [lit[29] 103° (1.3 mm),

n_D^{25} 1.5825]; nmr (CCl_4) 2.5-3.0 (m, 5, ArH), 5.6 (s, 2, CH_2), 5.8 (s, 1, O-H); ir (CCl_4) 3620 (w, free OH), 3500-3100 (m, bonded OH), 2230 (w, C≡C), 1600 (w, Ar), 1490 (s, Ar), 1030 (s, C-O), 680 (s, ArH).

B Phenylpropargyl Bromide (8)

Phenylpropargyl alcohol (13.2 g, 0.10 mole) and pyridine (0.5 ml) were dissolved in 50 ml of anhydrous ether in a 100 ml, three-necked, round-bottomed flask equipped with a magnetic stirrer, a reflux condenser (drying tube attached) and an addition funnel. The solution was cooled to 0° and phosphorous tribromide (11.4 g, 0.042 mole = 0.125 equiv)[30] was added dropwise at a rate sufficient to maintain a gentle reflux. The solution was stirred at reflux temperature for 2 hr, cooled to 25° and the upper layer was poured on cracked ice (200 g). The two layers were separated and the aqueous layer was extracted twice with 50 ml portions of ether. The combined ether extracts were washed three times with 50 ml portions of saturated, aqueous sodium bicarbonate and once with 100 ml of water. The ethereal layer was dried, concentrated and distilled yielding 15.5 g (80%) of phenylpropargyl bromide (8): bp 89-91° (1.0 mm); n_D^{25} 1.6194 [lit[29] 93° (1 mm), n_D^{25} 1.6195]; nmr (CCl_4) 2.5-3.0 (m, 5, ArH), 6.0 (s, 2, CH_2); ir (CCl_4) 2205 (m, C≡C), 1600 (w, Ar), 1490 (m, Ar), 1200 (s, C-Br), 690 (s, ArH), 605 (m), 520 (w), 440 (w).

C 1,1,4-Triphenylbutyn-1-ol (10)

Magnesium turnings (3.0 g, 0.12 mole) were covered with 150 ml of anhydrous ether in a one litre, three-necked, Morton flask fitted with a mechanical stirrer, a reflux condenser (drying tube attached) and an addition funnel. Phenylpropargyl bromide (24.0 g, 0.12 mole) dissolved in 75 ml of anhydrous ether was added dropwise at a rate sufficient to maintain a gentle reflux. After addition of the solution, the mixture was stirred at reflux temperature for 1 hr and cooled to 0°. A solution of benzophenone (21.0 g, 0.12 mole) in 100 ml of anhydrous ether was added dropwise and the solution was stirred for 15 hr. The solution was cooled to 0° and hydrolyzed by the addition of 100 ml of saturated, aqueous ammonium chloride. The two layers were separated, and the aqueous layer was extracted twice with 100 ml portions of ether. The combined ether layers were washed twice with 100 ml portions of saturated, aqueous sodium bicarbonate, and twice with 100 ml portions of water. The ethereal layer was dried and concentrated, yielding 32 g of a gummy, orange oil. Infra-red analysis of the crude oil showed the presence of an alcohol (3600), a ketone (1660) and presumably an allene (1950) and an acetylene (2205). An attempted separation of this apparent mixture of materials by column chromatography (neutral alumina, Brockman activity 1) failed, as did attempted recrystallizations of the crude oil. Attempts to distill the material were partially successful,

but at great loss of material. From 15 g of crude product only 0.5 g of semi-pure 10 could be obtained. Therefore, the following procedure was employed. Crude product (5.0 g) was placed in a 300 ml Erlenmeyer flask, covered with 200 ml heptane and the solution was refluxed for 5 min. This resulted in a cloudy, yellow solution and a solid, black residue. The solution was decanted from the residue and cooled to 0°. This resulted in a clear solution plus more solid residue. The solution was decanted from the residue and after standing several hours, yielded 0.6 g (9%) of crystalline 1,1,4-triphenylbutyn-1-ol (10): mp 89-91°; nmr ($CDCl_3$) 2.4-2.8 (m, 15, ArH), 6.6 (s, 2, CH_2), 6.9 (s, 1, O-H); ir (CCl_4) 3580 (m, bonded OH), 3100-3000 (m, ArH), 1600 (w, Ar), 1490 (s, Ar), 1450 (s, Ar), 1162 (m, C-O), 1050 (m), 1025 (m), 1000 (m), 690 (s, ArH), 600 (s).

Anal. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 89.03; H, 6.25.

Synthesis of Authentic Phenylallene (13)

The method developed by Doering and LaFlamme[17] (Figure 7) was applied here. First attempted was the reaction of the 1,1-dichloro-2-phenylcyclopropane with n-butyllithium. The second attempt involved the reaction of 1,1-dibromo-2-phenylcyclopropane with magnesium metal (Figure 18).

A1 1,1-Dichloro-2-phenylcyclopropane

This compound was prepared according to the procedure of Dale and Schwartzentruber.[27] Thus, 56 g of styrene (0.54 mole), 28 g of potassium t-butoxide (0.25 mole) and 30 g of chloroform (0.25 mole) yielded 25 g (52%) of 1,1-dichloro-2-phenylcyclopropane: bp 53-55° (0.3 mm); n_D^{25} 1.5500 [lit[27] 78-83° (2 mm), n_D^{25} 1.5498]; nmr (CCl_4) 2.8 (s, 5, ArH), 7.0-7.4 (t, 1, J = 9.5 Hz, CH), 7.9-8.3 (m, 2, CH_2). The ir spectrum was in good agreement with the literature.[27]

A2 1,1-Dibromo-2-phenylcyclopropane (20)

This compound was prepared in the exact same manner as its chlorine analogue with the exception that 63.2 g of bromoform (0.25 mole) was used in place of chloroform, yielding 34 g (50%) of 1,1-dibromo-2-phenylcyclopropane (20): bp 85-87° (0.3 mm); n_D^{25} 1.5983 [lit[27] 97° (1 mm), n_D^{25} 1.5988]; nmr (CCl_4) 2.8 (s, 5, ArH), 6.9-7.3 (t, 1, J = 9.5 Hz, CH), 7.8-8.2 (m, 2, CH_2). The ir spectrum was in good agreement with the literature.[27]

B Phenylallene (13)

1 Reaction of 1,1-Dichloro-2-phenylcyclopropane with n-Butyllithium

A solution of 1,1-dichloro-2-phenylcyclopropane (9.34 g,

0.05 mole) in 60 ml of anhydrous ether was placed in a 100 ml, four-necked, round-bottomed flask fitted with a mechanical stirrer, a reflux condenser (nitrogen inlet attached), a thermometer well and a dropping funnel. The solution was cooled in a Dry Ice-ethanol bath and n-butyllithium (3.2 g, 0.05 mole) was added dropwise (as a 20% solution in hexane).[26] The solution was stirred for 1 hr and warmed to 0°. The reaction was terminated by the dropwise addition of 200 ml of water and the two layers which resulted were separated. The aqueous layer was extracted with two 50 ml portions of ether and the combined organic layers were washed twice with 50 ml portions of water. The organic layer was dried and concentrated giving 6 g of a dark red oil. Infra-red analysis of the crude oil showed the presence of a small amount of an allene (1950) and a large amount of a terminal acetylene (3300, 2100). Repetition of this entire procedure produced similar results and this route to phenylallene was abandoned.

2 Reaction of 1,1-Dibromo-2-phenylcyclopropane with Magnesium Metal

Magnesium turnings (1.22 g, 0.05 mole) were covered with 20 ml of anhydrous ether in a three-necked, 100 ml, round-bottomed flask fitted with a reflux condenser (drying tube attached), a magnetic stirrer, a nitrogen inlet and an

addition funnel. 1,1-Dibromo-2-phenylcyclopropane (13.8 g, 0.05 mole) was added dropwise at a rate sufficient to maintain a gentle reflux. After addition of the halide, the solution was stirred at reflux temperature for 2 hr and cooled in an ice bath. The reaction was terminated by the dropwise addition of 20 ml of water. The two layers were separated and the aqueous layer was extracted three times with 25 ml portions of ether. The combined ether layers were washed twice with 50 ml portions of water. The ethereal layer was then dried, concentrated and distilled twice yielding 3.1 g (54%) of phenylallene (13): bp 72-74° (16 mm); n_D^{25} 1.5730 [lit[4] 68° (16 mm), n_D^{25} 1.5830]; nmr (CCl_4) 2.8 (s, 5, ArH). 3.8-4.0 (t, 1, J = 9 Hz, CH), 4.9-5.1 (d, 2, J = 9 Hz, CH_2); ir (CCl_4) 3100-3000 (m, ArH), 1945 (s, C=C=C), 1600 (m, Ar), 1495 (s, Ar), 1450 (m, Ar), 1030 (w), 910 (s), 870 (s), 850 (s, $=CH_2$), 700 (s), 630 (s), 600 (w, ArH), 440 (m).

Reaction of Phenylpropargyl Magnesium Bromide (9) with Water

Magnesium turnings (1.22 g, 0.05 mole) were covered with 30 ml of anhydrous ether in a 100 ml, three-necked Morton flask fitted with a magnetic stirrer, a reflux condenser (nitrogen inlet attached) and a dropping funnel. A solution of phenylpropargyl bromide (5.8 g, 0.03 mole) in 25 ml anhydrous ether was added dropwise at a rate sufficient to maintain a gentle reflux. After addition of the bromide,

the solution was stirred at 25° for 2 hr. The solution was cooled to 20° and water (25 g, 1.4 mole) was added dropwise. The two layers were separated and the aqueous layer was extracted twice with 50 ml portions of ether. The ether layer was washed twice with 50 ml portions of water, dried and concentrated to a volume of about 7 ml. The concentrate was subjected to glc analysis (column f, 70°) which showed two components to be present (besides solvent) in approximately equal proportions. Preparative glc (column f, 110°, 2 cc He/sec) was used to recover enough of each component for identification by ir and nmr spectra. The first component gave spectra identical to those of phenylallene (13) (Figure 15). The second component gave spectra compatible with the other expected product of the reaction, phenylmethylacetylene (12): nmr (CCl_4) 2.5-2.8 (s, 5, Ar<u>H</u>), 8.0 (s, 3, $C\underline{H}_3$); ir (CCl_4) 3100-3000 (m, ArH), 2920 (m, CH_3), 2840 (m, CH_3), 2250 (w, C≡C), 1600 (m, Ar), 1490 (s, Ar), 1440 (m, Ar), 1070 (m), 1030 (m), 910 (m), 695 (s, ArH), 525 (s).

Pyrolysis of 1,1,4-Triphenylbutyn-1-ol

A Pyrolysis in the Gas Chromatographic Instrument

A saturated solution of the alcohol (10) in chloroform was injected into the glc instrument under standard conditions. Pyrolysis was assumed to take place immediately on the injection port. Columns a, b and c were used (at 250°,

70-250° and 70-180°, respectively) to identify phenylallene (13) and benzophenone (21) by comparison of their retention times with those of authentic samples. Columns d, e and f were used (at 70-280°, 250° and 150-175°, respectively) for the preparative glc of the pyrolysate. The separated pyrolysate components collected in this manner were subjected to ir and nmr analysis and where possible, the spectra produced were compared with those of authentic samples. A total of five components were detected, separated and collected. It was impossible to measure the amount of each component formed since separation and collection of all components could not be carried out on a single glc column. The components appeared to be produced in the following proportions: 22>>21>12>13>23. The first and third components were the expected products phenylallene (13) (Figure 19) and benzophenone (21). The second component appeared to be phenylmethylacetylene (12) as its spectra were identical to those of 12 produced in the reaction of 9 with water. The allene (13) and the acetylene (12) were in approximately a 30:70 ratio, and it was shown that 13 would not isomerize to 12 or vice versa (under the pyrolysis conditions) by the following procedure. Authentic, pure 12 and pure 13 were each separately injected, collected and reinjected in the glc under the pyrolysis conditions. There was no formation of new components, or formation of 12 from 13, or formation of 13 from 12 detected on either pass of either component through the glc. The fourth component was

produced in the largest amount of all five, and spectral analysis indicated it to be 1,1,4-triphenylbutyene (22): nmr (CCl_4) 2.5-3.0 (m, 15, ArH), 3.9 (s, 1, CH); ir (CCl_4) 3100-3000 (m, ArH), 1600 (m, Ar), 1500 (m, Ar), 1490 (m, Ar), 1440 (m, Ar), 1030 (m), 850 (w), 700 (s, ArH), 530 (w). The fifth component (23) was in too minor an amount and was too contaminated with 22 (the glc separation was poor here) to be identified: nmr (CCl_4) 2.3-3.0 (m, 32, ArH), 3.3 (s, 1); ir (CCl_4) 3100-3000 (m, ArH), 1600 (w, Ar), 1490 (m, Ar), 1440 (w, Ar), 1030 (m), 700 (s, ArH).

B Pyrolysis in the Neat

The apparatus shown in Figure 22 was used for these pyrolyses. A small amount of the alcohol (10) (0.5 g, 1.7 mmole) was placed in tube A. The apparatus was con-

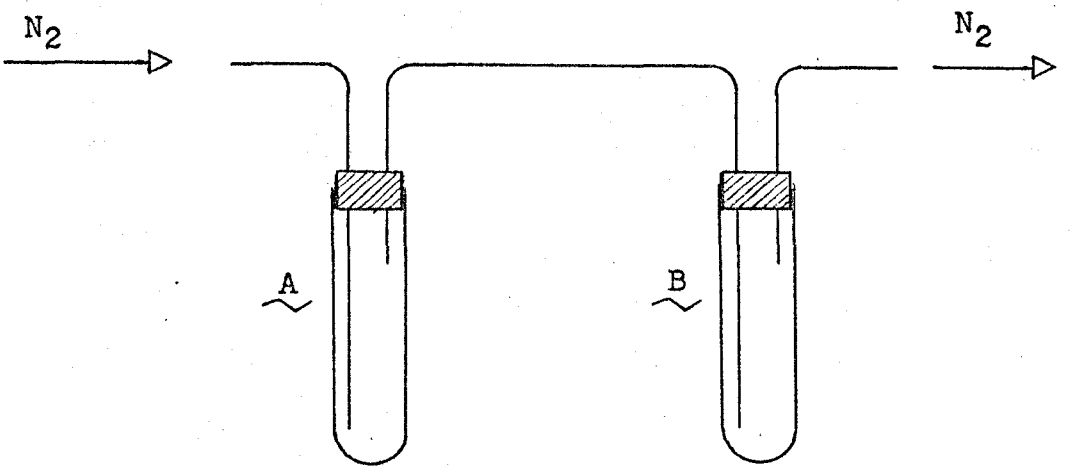


Figure 22 - Apparatus for Pyrolysis in the Neat

nected and the nitrogen flow was started. Tube A was immersed in an oil bath (preheated to the desired temperature) and simultaneously tube B was immersed in liquid nitrogen. The tubes were held in these positions for the desired length of time, removed and cooled to 25°. Both the residue in tube A and the condensate in tube B were divided into pentane soluble and insoluble fractions (to partially separate the unreacted alcohol). These fractions were analyzed by preparative and analytical thin layer chromatography (tlc), (benzene on silica gel), and by ir spectra. Temperatures and times used were: 225°/2 hr, 230°/7 hr and 250°/1 hr. In all cases the results were essentially the same. Tube B was found to contain only benzophenone (21) (plus some traces of 10 carried over by the nitrogen flow). Tube A was found to contain 10, 21 and an unknown compound which fluoresced under ultra violet (uv) light (3660 Å, 2537 Å). The infra-red spectrum (CCl_4) contained bands at 3300 (w, ≡C-H), 3100-3000 (m, ArH), 3000-2850 (s, aliph C-H), 1710 (w), 1600 (w, Ar), 1490 (m, Ar), 1420 (w), 1250 (m), 1210 (w), 1100-1000 (m), 870 (m), 690 (s, ArH). Insufficient sample (2 mg) was recovered for any further examination. In no case was any phenylallene detected by either ir or tlc.

C Pyrolysis in Solvents

1 Nitrobenzene Solvent

A solution of 10 (130 mg, 0.4 mmole) in 5 ml of freshly

distilled nitrobenzene was placed in a one-necked, 10 ml round-bottomed flask fitted with a reflux condenser (nitrogen inlet attached) and a magnetic stirrer. The solution was stirred at reflux temperature (211°) for 24 hr and the progress of the pyrolysis was monitored by tlc (benzene on silica gel). Only trace amounts of decomposition occurred and no phenylallene was detected.

2 N,N-Dimethylformamide Solvent

A solution 10 (100 mg, 0.3 mmole) in 4 ml of N,N-dimethylformamide (DMF)[31] was placed in a 10 ml, one-necked, round-bottomed flask fitted with a reflux condenser (nitrogen inlet attached) and a magnetic stirrer. To this was added 4-bromonitrobenzene (0.3 g, 1.5 mmole) which, it was hoped, would act as a carbanion trapping agent. The solution was stirred at reflux temperature (153°) for 24 hr and monitored by tlc (benzene on silica gel). By the end of the 24 hr period, the starting material had completely decomposed and there were several new materials present. There was, however, no detectable phenylallene. Separation of these components by preparative tlc (benzene on silica gel) yielded three major components in recoverable amounts. One of these components ($R_f \sim .7$) was unreacted 4-bromonitrobenzene, while of the other two, one ($R_f \sim .9$) fluoresced brightly under uv light (3660 Å, 2537 Å). When isolated from the silica gel, 32 mg of this material was obtained. This material was shown to be impure by analytical

tlc (benzene on silica gel, ether on silica, petroleum ether on silica gel). Attempts to purify this material by preparative tlc failed. Spectral properties of this material were as follows: nmr ($CDCl_3$) 2.5-3.0 (m, 16, Ar<u>H</u>), 3.9 (s, 1), 8.8 (s, 4), 9.0-9.3 (m, 3); ir ($CHCl_3$) 3100-3000 (m, ArH), 3000-2850 (m, aliph CH), 1710 (m), 1600 (w, Ar), 1490 (m, Ar), 1440 (m, Ar), 1350 (m), 1060 (m), 690 (s, ArH), 560 (m), 520 (m).

The remaining component ($R_f \sim .1$) did not fluoresce under uv light and when isolated from the silica gel, yielded 50 mg of material which was shown to be impure by analytical tlc (benzene on silica gel, ether on silica gel, petroleum ether on silica gel). Attempts to purify this material by preparative tlc failed. Spectral properties of this material were as follows: nmr ($CDCl_3$) 2.9 (s, 8, Ar<u>H</u>), 6.9 (s, 1), 7.1 (d, 1, $\underline{J}$ = 7 Hz), 8.8 (s, 6), 9.0-9.3 (m, 3); ir ($CHCl_3$) 3100-3000 (w, ArH), 3000-2850 (m, aliph CH), 1600 (m, Ar), 1490 (w, Ar), 1320 (m), 1100 (m).

3 <u>Bis</u>(2-Methoxyethyl) Ether Solvent

A solution of <u>10</u> (100 mg, 0.3 mmole) in 10 ml of <u>bis</u>(2-methoxyethyl) ether (Diglyme)[32] was placed in a 25 ml, one-necked, round-bottomed flask fitted with a reflux condenser (nitrogen inlet attached) and a magnetic stirrer. To this was added picryl chloride (300 mg, 1.2 mmole) which, it was hoped, would act as a carbanion

trapping agent. Two identical control set-ups were also used. The first however contained no 10, and the second omitted the picryl chloride. All three systems were stirred for 24 hr at reflux temperature (164°) and the pyrolysis was monitored by tlc (25% ether/75% benzene on silica gel). At the end of the 24 hr period, tlc indicated that no appreciable decomposition of 10 had occurred and that no phenylallene was formed.

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PART II

THE PYROLYSIS OF THE HYDROGEN- AND METHYL PHTHALATE ESTERS OF THE *cis*- AND *trans*-1,2-DIMETHYLCYCLOHEXANOLS

CHAPTER I

INTRODUCTION

The pyrolysis of esters, usually in the gas phase at temperatures of 300-550°, is a reaction of synthetic utility for the introduction of points of unsaturation. This usefulness is derived from the facts that only simple equipment and procedures are necessary, the work-up of products is relatively simple and the yields are usually good. Furthermore, the products are quite predictable as a result of the high degree of *cis* stereospecificity of the elimination and the low degree of product rearrangement under the pyrolysis conditions.[1]

These unusual characteristics of ester pyrolyses have made them the subject of extensive investigations along two major lines. The stereochemistry of the elimination has been examined and was found to be almost exclusively *cis*. The direction of the elimination has been studied and was found to be dependent to varying degrees on

statistical effects, steric effects and thermodynamic effects.[1] Observations of this type led Hurd and Blunck[2] to propose a six-membered, cyclic, hydrogen-bridged transition state for these pyrolyses (Figure 1). This

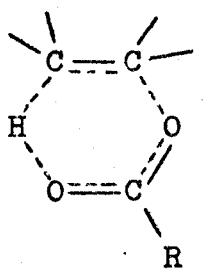
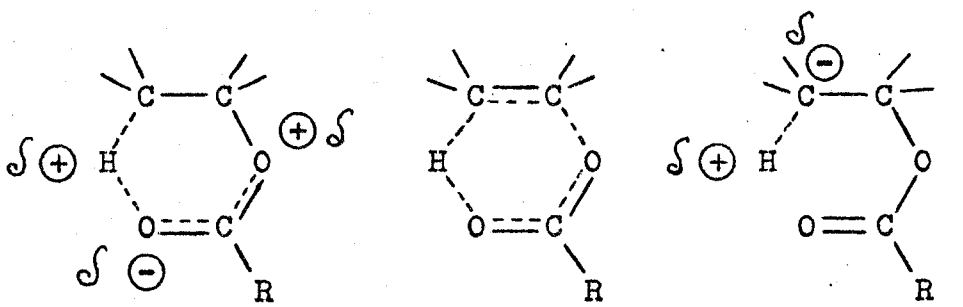


Figure 1 - Hurd and Blunck Transition State

transition state, the one described later by DePuy and King[1] (which allowed for a very small degree of charge development), and those pictured by Banthorpe (Figure 2)[3]



A — E2-Like "Heterolytic"

B — Concerted "Homolytic"

C — E1cB-Like "Heterolytic"

Figure 2 - Banthorpe's Transition States

are all very similar in nature, and account for several of the significant characteristics of ester pyrolysis. These include the cis character of the elimination, the unimolecularity of the reaction, the usually observed small negative entropy of activation and primary kinetic isotope effects. These transition states are not, however, completely satisfactory. They do not account for several significant observations and trends in ester pyrolysis.

Bailey and Hewitt[4] have demonstrated that the rate of pyrolysis of esters is directly dependent upon the strength of the parent acid from which the ester is derived, thus indicating that the ability of the carboxylate moiety to leave with an electron pair is important in the rate-determining step.

Williams et al.[5] have shown that the rate of pyrolysis of esters proceeds in the relative order of the carbonium ion stability of the hydrocarbon portion of the molecule. That is, esters of tertiary alcohols were found to pyrolyze at a greater rate than those of secondary alcohols, which in turn pyrolyzed faster than those of primary alcohols. This, in conjunction with the work of Bailey and Hewitt,[4] indicates the possibility of some heterolysis of the alkyl-oxygen bond in the rate-determining step of ester pyrolysis.

This line of thinking found some support in the work of O'Conner and Nace[6] on the pyrolysis of xanthates which, it is felt, probably pyrolyze via a mechanism similar to that of ester pyrolysis.[1] These authors obtained a Hammett

rho value of +0.87 (for the xanthate moiety), in the pyrolysis of cholesteryl xanthates, indicating a build-up of negative charge on the xanthate moiety.

The application of the Hammett equation to ester pyrolysis has been carried out by Taylor et al.,[7] and the results were in agreement with those of O'Conner and Nace.[6] Using various substituted α- and β-phenylated acetates (Figure 3), these authors calculated (using Brown's σ^+ values) a rho value of -0.66 for aryl substituents in the α position to the ester moiety, and a rho value of +0.30 for aryl substituents in the β position to the ester moiety.

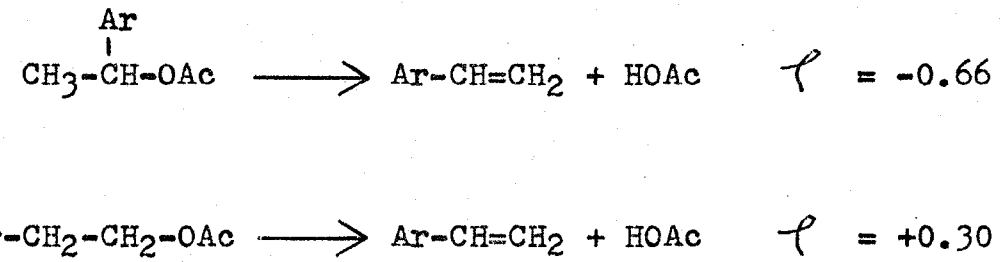


Figure 3 - Esters Pyrolyzed by Taylor et al. for Hammett Relationship

Furthermore, Smith et al.[8] have pyrolyzed substituted ethyl benzoates and obtained a rho value of +0.20 for the acid moiety (using Taft's σ^o values).

Thus, contrary to the Hurd mechanism, these results also support the concept of at least some heterolysis of the alkyl-oxygen bond in the rate-determining step of ester pyrolysis. A mechanism which is more consistent with these

results and which involves the formation of ion pairs has been proposed more recently by Scheer et al.[9] (Figure 4) on the basis of their work on the gas phase pyrolysis of twenty-eight α-alkyl substituted alkyl acetates (Table I).

$$R\text{-}OAc \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \left[R^{\oplus} \quad OAc^{\ominus} \right] \xrightarrow{k_2} \text{Olefins} + AcOH$$

Figure 4 - The Ionic Mechanism of Scheer et al.

Scheer et al. also point out that this mechanism can account for primary kinetic isotope effects if one assumes that the ion pair formation is reversible, and that the rate of return of the ion pair to starting material is greater than its rate of decomposition to olefins plus acid ($k_{-1} > k_2$). Furthermore, they point out that Maccoll[10] has suggested that the formation of such an ion pair is energetically feasible even in the gas phase providing that undissociated ion pairs are formed. The coulombic energy gained by having the fragments remain in close proximity to each other (approximately 2 Å) is sufficient (as much as 170 kcal/mole) to lower the energy requirements for heterolysis to an acceptable level.

This ion pair mechanism of Scheer et al.[9] takes on more meaning when a transition state for the formation of the ion pair is pictured. Maccoll[11] has postulated a transition state for the pyrolysis of esters which appears suitable for this

TABLE I

Activation Parameters of Selected Acetates

Acetate	E_{exp} (kcal/mole)	S# (eu)	T (°C)
Ethyl	46.5	-7.0	487.8
n-Propyl	46.2	-7.6	486.4
iso-Propyl	45.2	-2.9	408.5
n-Butyl	44.5	-9.3	481.5
2-Butyl	47.0	+0.6	404.7
tert-Butyl	42.4	+2.6	322.7
n-Pentyl	44.9	-8.7	473.3
2-Pentyl	42.3	-5.9	409.3
tert-Amyl	43.1	+5.5	303.9
1-Methylcyclohexyl	44.0	+6.5	313.3

mechanism (Figure 5). Using this transition state in conjunction with the pyrolysis mechanism of Scheer et al.,[9] most of the known characteristics of ester pyrolysis may be rationalized. Thus, the observations of Skell and Hall,[12] who observed on the pyrolysis of sec-butyl acetate a β - deuterium kinetic isotope effect of $k_H/k_D = 1.7$, as well as stereospecific cis elimination, are consistent with an ion

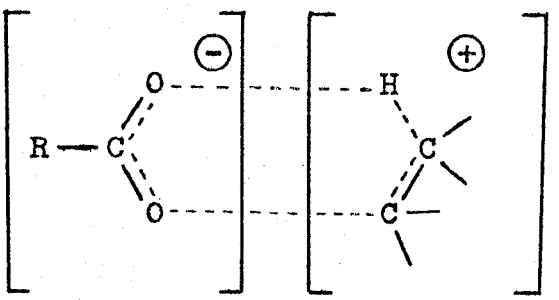


Figure 5 - Maccoll Transition State

pair mechanism and are not necessarily compatible only with the Hurd and Blunck mechanism.

Support for the postulates of Scheer et al.[9] and Maccoll[11] was given by the work of Rutherford and Fung[12] on the neat pyrolysis of some tertiary hydrogen phthalate esters. Carbonium ion character was felt to be evident in these pyrolyses as shown by trends in product distributions, and especially the observation of 19% trans elimination in the pyrolysis of trans-1,2-dimethylcyclohexyl hydrogen phthalate (Figure 6). Such trans elimination is not allowed

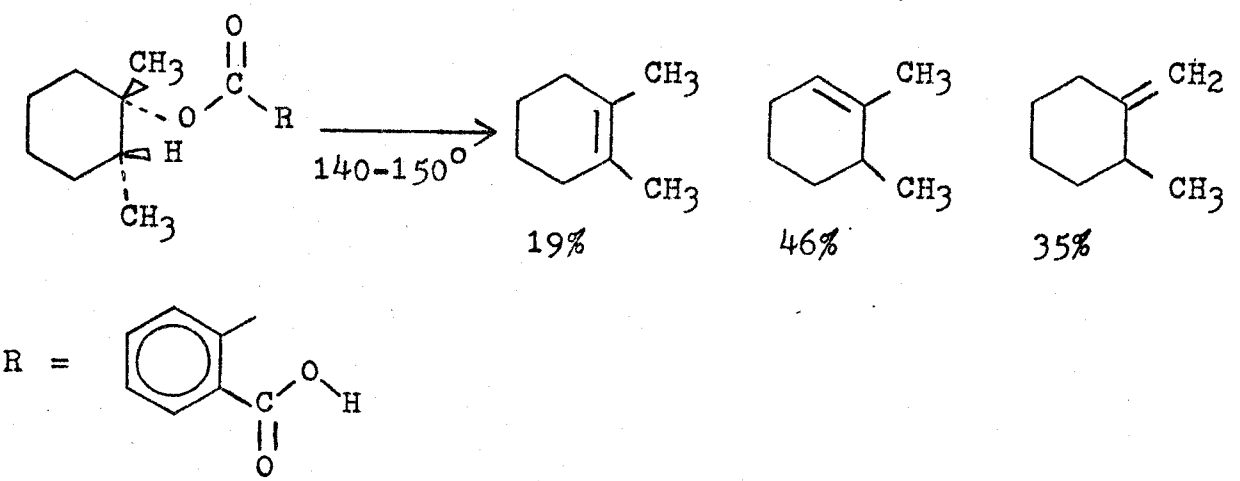


Figure 6 - Products From the Neat Pyrolysis of trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate

by a planar, six-membered, cyclic transition state such as Hurd and Blunck have proposed unless an unfavourable (from considerations of nonplanarity) diequatorial (e,e) elimination takes place. Since this (e,e elimination) did not occur in the pyrolysis of trans-1,2-dimethylcyclohexyl acetate,[14] it is unlikely that it occurred in the pyrolysis of the hydrogen phthalate ester of the same alcohol.

The pyrolysis of this same hydrogen phthalate ester was examined further by Rutherford and Ottenbrite.[15] Using the ^{18}O labelled ester in a manner analogous to that used by Goering and Pombo[16] to follow the solvolysis of an allylic ester, these authors demonstrated that reversible bond breaking was occurring during the pyrolysis of trans-1,2-dimethylcyclohexyl hydrogen phthalate ester (Figure 7).

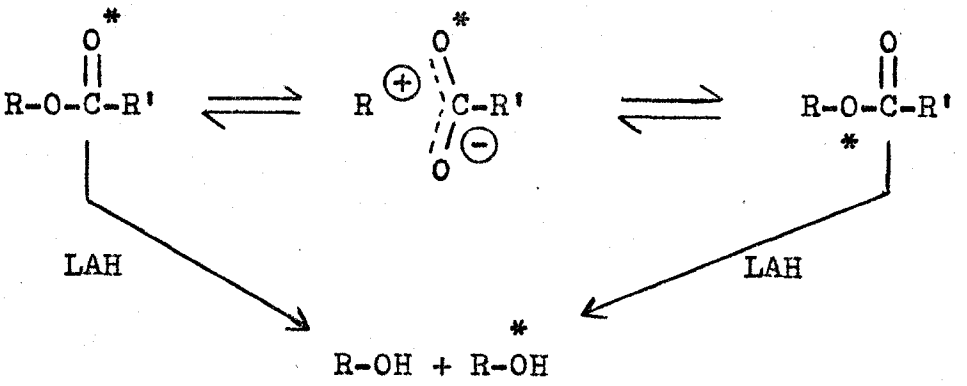


Figure 7 - Isotope Exchange Study of the Neat Pyrolysis of trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate

The observed 17% (minimum) exchange provided the first solid chemical evidence for an ester pyrolysis mechanism involving

the reversible formation of an ion pair.

The necessary kinetic evidence to support such a mechanism for the pyrolysis of this ester was provided by Wassenaar,[17] who studied the kinetics and product distributions from the neat pyrolysis of both cis- and trans-1,2-dimethylcyclohexyl hydrogen phthalate esters. The activation parameters (Table II) were in good agreement with what would be predicted on the basis of a mechanism involving the rate-determining formation of an ion pair intermediate. That is, the entropies of activation (6 ± 4 eu for the trans-ester and 10 ± 1 eu for the cis-ester) are quite consistent with

TABLE II

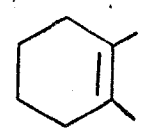
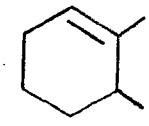
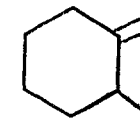
Activation Parameters for the Neat Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate Esters

Compound	E_{exp} (kcal/mole)	A (sec^{-1} x 10^{13})	$\Delta S^{\#}$ (eu)
trans	32.7 ± 1.6	47.51	6 ± 4
cis	33.7 ± 0.5	343.8	10 ± 1

the increase in randomness expected for the formation of a nonsolvated ion pair (in each case). Similarly, the product distributions indicate that in each case the product determining intermediate is an ion pair. This is a result of the fact that anion proximity (to the hydrogens to be removed) effects appear to determine the relative distribution of olefins from each ester.[17]

TABLE III

Product Distributions From the Neat Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate Esters

Compound	Product %		
			
trans	24	46	30
cis	56	20	24

In support of such an ion pair intermediate, Wassenaar[17] suggested that the proton of the ortho-carboxyl function was participating in these pyrolyses in such a manner as to enhance the leaving group ability of the phthalate moiety (Figure 8). Such participation could account (in part) for the relatively low energies of activation observed (Table II) in the pyrolysis of these esters.

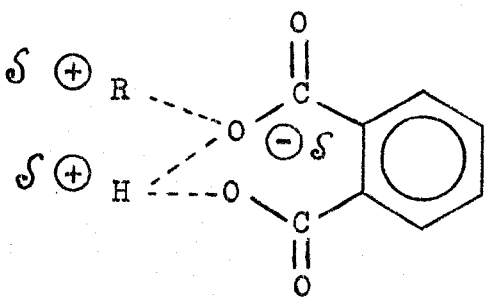


Figure 8 - Proposed ortho-Carboxyl Hydrogen Participation

In a further attempt to demonstrate carbonium ion character in the pyrolysis of these esters, their α-phenyl analogues, cis- and trans-1-phenyl-2-methylcyclohexyl hydrogen phthalate were pyrolyzed in N,N-dimethylformamide (DMF).[17] At first appearance, the results of the kinetic study (Table IV) produced more confusion than support for an ion pair mechanism as the negative entropy of activation for the trans ester pyrolysis suggested decomposition by a cyclic mechanism. The absence of primary kinetic isotope effects ($k_H/k_D = 1.02$)[17]

TABLE IV

Activation Parameters for the Pyrolysis of cis- and trans-1-Phenyl-2-Methylcyclohexyl Hydrogen Phthalate Esters in N,N-Dimethylformamide

Compound	E_{exp} (kcal/mole)	A (sec^{-1})	$\Delta S^{\#}$ (eu)
trans	26.2 ± 1.6	79.06×10^{11}	-11 ± 4
cis	32.7 ± 1.4	92.04×10^{13}	7 ± 4

in the pyrolysis of the 2,6,6-trideuterated trans-ester indicated that this was not so. Therefore, the results were interpreted as evidence for the rate-determining formation of a solvent-separated ion pair in the case of the trans-ester, while the cis-ester pyrolyzed via an intimate ion pair which decomposed too rapidly to generate the solvent-separated ion pair.

The rationale and summation of the above results may be best reconciled using the general reaction scheme shown in Figure 9. This scheme is essentially a modification and expansion of an ion pair scheme originally proposed by Winstein and co-workers[18] to explain behaviour observed in

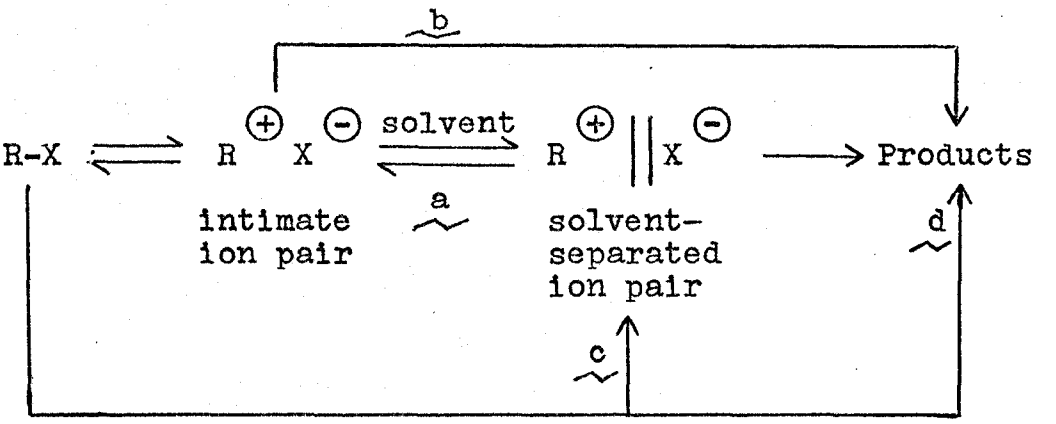


Figure 9 - A Proposed Generalized Reaction Scheme for the Pyrolysis of Esters

solvolysis chemistry. Thus there are four paths by which starting material may proceed to products. In path a, an intimate ion pair is followed by a solvent-separated ion pair from which elimination to form products occurs. In path b, elimination occurs directly from the intimate ion pair while in path c, the solvent-separated ion pair, from which elimination occurs, is formed without the intervention of the intimate ion pair. Finally, in path d, elimination occurs directly from the starting material without the intervention of any intermediates. The neat pyrolysis of both cis- and trans-1,2-dimethylcyclohexyl hydrogen phthalate esters would be best explained by paths a and/or b. Similarly, the pyrolysis in DMF of cis-1-phenyl-2-methylcyclohexyl hydrogen phthalate appears to follow paths a and/or b, while the trans-epimer appears to decompose via paths a and/or c. These suggestions are not meant to preclude a certain degree

of participation of mixed mechanisms, as the above discussed results are not sufficient to warrant such rigorous conclusions.

Because of the questions which arise when one attempts to place exact interpretations on the above results, a great deal of further work on the pyrolysis of such esters is required. In the case of the neat pyrolysis of cis- and trans-1,2-dimethylcyclohexyl hydrogen phthalate esters, there are two general areas to be studied. First, the postulate of ortho-carboxyl proton participation should be tested. Any evidence for the proposed participation would be important since such participation would be additional evidence for carbonium ion character in these pyrolyses, and also would explain (in part) the unique low temperature pyrolysis of these tertiary hydrogen phthalate esters. For this purpose, it was decided to carry out an investigation into the kinetics and product distributions of the neat pyrolysis of the corresponding methyl phthalate diesters.

Second, more information on the nature of the proposed ion pairs is necessary. Such information could perhaps be used to determine which pathway (Figure 9) predominates in the pyrolysis of these esters, and might allow a more detailed description of that pathway and the ion pair(s) involved. For this purpose it was decided to carry out quantitative isotope exchange and geometrical isomerization (conversion from cis to trans or vice versa) studies on the neat pyrolysis of these esters.

An obvious extension of this work would be an exactly

similar investigation into the pyrolysis of the cis- and trans-1,2-dimethylcyclohexyl hydrogen phthalate esters in DMF. Such a study should compliment and clarify the results from both the pyrolysis of these esters in the neat, and the pyrolysis of the 1-phenyl-2-methylcyclohexyl esters in DMF. Furthermore, the information gained from this study should greatly enhance our understanding of the nature of the solution pyrolysis of hydrogen phthalate esters. Thus, it was decided that kinetic, product distribution, isotope exchange, and geometrical isomerization studies would be carried out on the pyrolysis of the 1,2-dimethylcyclohexyl esters in DMF. In addition to this, it was decided to examine the pyrolysis of the corresponding methyl phthalate diesters in DMF in order to check for proton participation in the solution pyrolysis of the hydrogen phthalate esters.

The summation of the results of such investigations together with previous studies[17] as well as similar work carried out simultaneously in this laboratory[19] on the 1-phenyl-2-methylcyclohexyl esters should provide a reasonably rigorous test of the general reaction scheme for ester pyrolysis as proposed in Figure 9.

CHAPTER II

RESULTS AND DISCUSSION

Kinetic Studies on the Neat Pyrolysis of *cis*- and *trans*-1,2-Dimethylcyclohexyl Methyl Phthalate Diesters

The previously discussed kinetic studies of Wassenaar[17] (Table II), showed that the experimental activation energies for the neat pyrolysis of *cis*- and *trans*-1,2-dimethylcyclohexyl hydrogen phthalate esters were much lower (approximately 10 kcal/mole) than those reported (Table I)[9] for the pyrolysis of similar tertiary acetates. The author postulated that this was caused by the proton of the *ortho*-carboxyl group of the phthalate moiety participating in such a manner as to enhance the leaving group ability of the phthalate moiety as shown in Figure 8. This suggestion has been tested by an examination of the rates of pyrolysis of the corresponding methyl phthalate diesters. If proton participation does enhance the rate of decomposition of hydrogen phthalate esters, then replacement of the proton with a methyl group should result in a decrease of the relative rate of decomposition.

The pyrolysis of both methyl esters was carried out in essentially the same manner as was used by Wassenaar[17] in his kinetic studies on the neat pyrolysis of the hydrogen phthalate esters. Both esters were pyrolyzed at the maximum

temperatures employed in the hydrogen phthalate kinetics.[17] Appropriate changes were made in the calculations (Appendix I) to account for the facts that the starting material had no acidic function, and a mono-acid rather than a diacid was generated. The results are listed in Table V.

The observed three-hundredfold rate decrease (k^{**}/k^{*}) demonstrates that replacement of the acid proton with a methyl group has a significant effect on the decomposition of these esters. It should be noted however, that the rate constants for methyl ester pyrolysis (k^{*}) are only initial rate constants, calculated on the basis of about 10% decomposition. The reason for this involves the problem that after this point (10% decomposition), the pyrolysis appears to be autocatalyzed, perhaps by the increasing presence of the acidic pyrolysis product, methyl hydrogen phthalate. This may be seen in a plot of ln ester remaining vs time. Thus, after about 10% decomposition has occurred, a curve rather than a straight line results. As reaction time increases, the curvature becomes increasingly more pronounced until 100% decomposition has occurred. If this behaviour is the result of intermolecular acid catalysis by the methyl hydrogen phthalate, then it further demonstrates the importance of proton enhancement of the leaving group ability of the phthalate moiety.

Product Distribution Studies on the Neat Pyrolysis of *cis*- and *trans*-1,2-Dimethylcyclohexyl Methyl Phthalate Diesters

TABLE V

Kinetic Studies on The Neat Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Methyl Phthalate Diesters

Compound	Temp (°C)	Rate Constant k^{*} ($sec^{-1} \times 10^{6}$)	Rate Constant k^{**} ($sec^{-1} \times 10^{6}$)	Rate Ratio $\frac{k^{**}}{k^{*}}$	Number of Points	Percent Complete	Correlation Coefficient
trans	137.5	5.8 ± 0.1	1764 ± 42	304	13	11.2	0.9939
cis	130.0	6.0 ± 0.1	1761 ± 29	293	19	13.6	0.9882

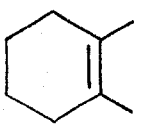
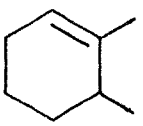
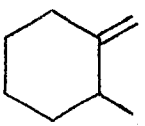
k^{*} = Rate constant for the pyrolysis of the methyl phthalate diester

k^{**} = Rate constant for the pyrolysis of the hydrogen phthalate ester

If the acid proton does play an important role in hydrogen phthalate ester pyrolysis, then this should be manifested not only in the rate constants observed for pyrolysis but also in the olefinic product distributions. This should be so since the absence of the acid proton in the methyl ester pyrolyses should result in the formation of a less ionic product-determining intermediate than would be expected from the hydrogen phthalate ester. This decrease in ionic character should manifest itself in a shift of the product distributions to a more Hofmann-like distribution than was observed in the hydrogen phthalate ester pyrolyses. The product distributions have been measured by gas chromatographic analysis (glc) of the olefinic products obtained upon neat pyrolysis of the diesters, and are reported in Table VI. A comparison of these product distributions with those previously reported by Wassenaar[17] for the pyrolysis of the hydrogen phthalate esters (Table III) shows that the expected shift to a more Hofmann-like product distribution is indeed observed, although the magnitude of the shift is relatively small. Again, it should be pointed out that these product distributions are only indicative of a trend and may not be regarded as exact since at least some of the olefinic products may have resulted from the previously postulated intermolecular acid catalyzed pyrolysis of these esters. Any contribution of this type of elimination could account for the relatively small magnitude of the shift towards a more Hofmann-like distribution.

TABLE VI

Product Distribution Studies on The Neat Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Methyl Phthalate Diesters

Compound	Temp (°C)	Duration (Min)	Product Distribution (%)		
					
trans	300	*	15.5	46.7	37.8
	200	5	25.0	49.9	25.1
	137	420	16.8	49.8	33.4
cis	300	*	44.6	24.5	30.9
	200	3	43.3	25.0	31.7
	130	420	45.0	23.2	31.8

* The duration of this pyrolysis is not known, as it was carried out in the gas chromatographic instrument.

In any event, both the large decrease in the initial rate of pyrolysis and the (small) change in the character of the product distribution observed when the ortho-carboxyl hydrogen is replaced by a methyl group support the aforementioned postulate of Wassenaar.[17]

Isotope Exchange Studies on the Neat Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate Esters

In order to further elucidate the nature of the postulated ion pair intermediates in the neat pyrolysis of these esters, it was decided to undertake a more exhaustive study of the isotope exchange as first observed by Rutherford and Ottenbrite.[15] Furthermore, in order to help determine which pathway is being followed (Figure 9) in the decomposition of these esters, it was decided to examine the partially pyrolyzed esters (that would be produced in isotope exchange studies) for geometrical isomerization. To this end, ^{18}O enriched cis- and trans-1,2-dimethylcyclohexyl hydrogen phthalate esters were prepared and partially pyrolyzed in the neat.

Essentially the same procedure as was used by Rutherford and Ottenbrite[15] was employed here with the exception that the esters were prepared with 11.0 atom per cent excess ^{18}O at each oxygen except the alkyl oxygen, which contained only the natural abundance (0.20%) of ^{18}O (Figure 10). The physical constants and spectra of the labelled esters were identical to those of the unlabelled esters. The esters were pyrolyzed employing

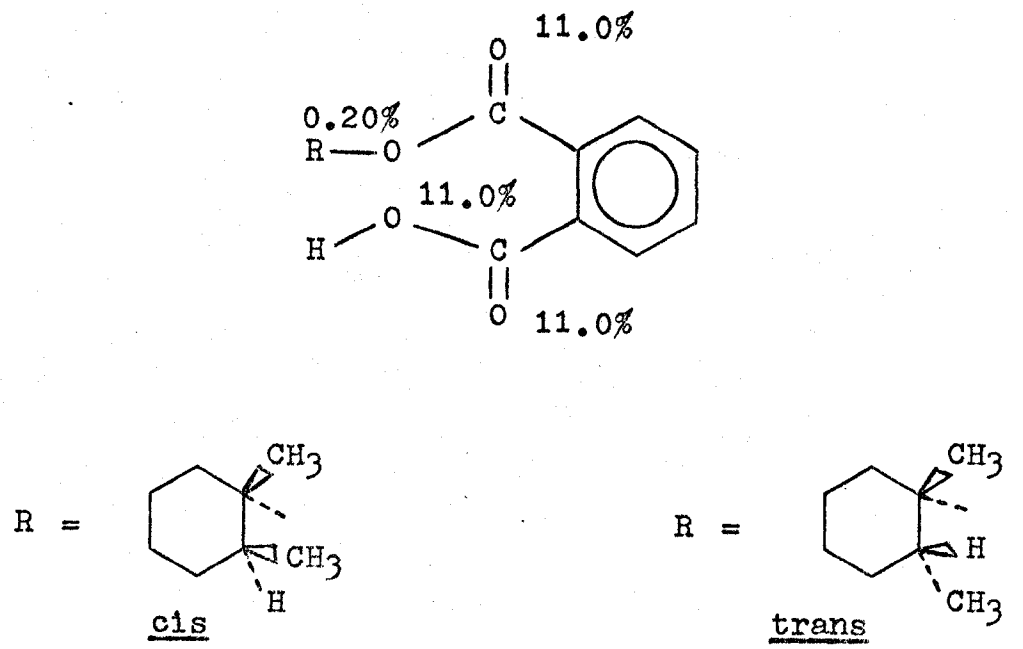


Figure 10 - ^{18}O Enriched cis- and trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate

the same apparatus as was used for the kinetic studies,[17] for lengths of time calculated (Appendix II) to result in 0, 20 and 70% pyrolysis. The unpyrolyzed esters were recovered, purified and reduced to the alcohols with lithium aluminum hydride (LAH). The cyclohexanols which resulted were separated from the other reduction product w,w'-dihydroxy-o-xylene (DHX) and were analyzed by glc for geometrical isomerization (Table VII), and by mass spectrometry (ms) for ^{18}O content (Table VIII).

Before discussion of the results, it should be pointed out just what any geometrical isomerization would mean. Geometrical isomerization of the hydrogen phthalate esters

TABLE VII

Geometrical Isomerization in the Neat Partial Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate Esters

Compound	Temp (°C)	Duration (min)	Per Cent Decomposition	Per Cent Isomerization
trans	-	-	0.0	0.0
	134.4	2.5	20.0	3.1
	134.4	13.5	70.0	3.7
cis	-	-	0.0	0.0
	120.0	6.1	20.0	0.0
	120.0	33.5	70.0	1.9

in the melt during pyrolysis would have to involve some form of reversible breakage of the alkyl-oxygen bond, leading to an intermediate in which the fragments are sufficiently free to allow the phthalate moiety to return to the opposite side of the cyclohexyl moiety from which it left. In the reaction scheme envisaged (Figure 9), this intermediate would have to be either a solvent-separated ion pair or an exceptionally

TABLE VIII

^{18}O Incorporation in The Neat Partial Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate Esters

Compound	Temp (°C)	Duration (Min)	Percent Decomp	M+2/M (%)	$^{18}O/O_{Ttl}$ (%)	Percent Exchange
trans	-	-	0.0	.590	.233	0.0
	134.4	2.5	20.0	.838[a] .697[b] .562[c]	.483 .343 .209	2.04*
	134.4	13.5	70.0	2.105 1.914 1.739	1.721 1.540 1.366	24.21*
cis	-	-	0.0	.570	.215	0.0
	120.0	6.1	20.0	.836 .795 .754	.480 .439 .398	4.14* 2.76**
	120.0	33.5	70.0	2.540 2.220 1.809	2.138 1.830 1.437	29.86* 19.91**

* based on "two-oxygen equilibration" ** based on"four-oxygen equilibration"
a = Maximum Value, b = Best Value, c = Minimum Value. All ^{18}O incorporation values will henceforth be reported in this manner.

loose intimate ion pair. The latter would be much less likely, albeit not impossible as shown by Goering's recent work with α-p-anisylethyl-p-nitrobenzoate where an intimate ion pair produced during solvolysis was sufficiently loose to allow racemization.[20]

It is evident from Table VII that the amount of isomerization is very small and perhaps negligible in all cases. The amount of isomerization was determined by glc analysis of the alcohols produced and, as such, was subject to all the errors inherent in that technique. Poor resolution of peaks and inseparable contaminants produced a poor base-line so that the errors resulting from integration of the alcohol peaks might well be larger than the calculated amount of isomerization. Therefore, the calculated per cent isomerization may be regarded only as an upper limit. The actual amount of opposite isomer present may in fact be much less or even zero. In any case, the amount of isomerization is very small.

If one assumes that reversible formation of a solvent-separated ion pair must result in geometrical isomerization, and that reversible formation of an intimate ion pair will not lead to isomerization, then it follows that there must be little or no reversible formation of solvent-separated ion pairs in these pyrolyses. This conclusion is in agreement with both the kinetic and product studies (of Wassenaar[17]) on this system. These studies indicated that formation of an intimate ion pair was the rate-determining step, and that

the intimate ion pair was the product-determining intermediate, thus leaving no room for a solvent-separated ion pair to become involved.

Table VIII lists the calculated per cent ^{18}O contents in the alcohols, and the per cent exchange values. The 0% decomposition values show that the method used does not introduce any extraneous ^{18}O incorporation. The 20 and 70% decomposition values show that for both esters, time dependent ^{18}O exchange does occur and therefore, reversible bond breakage must occur during the neat pyrolysis of both of these esters. Furthermore, an intermediate which allows oxygen equilibration to occur must be produced by this bond breakage. This intermediate would appear to be best envisaged as an intimate ion pair in both cases.

Further information about the ion pair formed in each case may be gained from a more detailed examination of the per cent ^{18}O incorporation values. For both 20 and 70% pyrolyses, the cis-alcohol (from the LAH reduction of the remaining ester) contains more ^{18}O than the trans-alcohol. There are several possible causes for this behaviour. Since it is felt that we are dealing with intimate ion pairs in both cases, it is possible that the cis-ion pair is looser and/or more ionic than the trans-ion pair, thus allowing for more free oxygen equilibration which would result in a greater ^{18}O incorporation. There is support for this suggestion in the kinetics previously done on this system, where it was shown that the entropies of activation were

6 ± 4 eu for the trans-ester pyrolysis, and 10 ± 1 eu for the cis-ester pyrolysis. This small but real difference indicates that there is a greater increase in randomness in going from the ground state to the transition state for the cis-ester than for the trans-ester. If it is assumed that both esters have approximately the same level of randomness in the ground state, then it follows that the transition state for the rate-determining step in the pyrolysis of the cis-ester is looser, or has a greater degree of randomness than in the case of the trans-ester. Since it is probable that the rate-determining step is the formation of an intimate ion pair in both cases, then this relative looseness should be reflected in the intimate ion pairs that result, and which are felt to be the source of the isotope exchange. Thus, one would expect that the cis-ester should show a greater ^{18}O incorporation than the trans-ester. An alternative explanation of these results may be that the cis-ester merely undergoes the total process of ionization, exchange and return to a greater overall degree than the trans-ester. Thus, a difference in the character of the ion pairs, though expected on the basis of kinetic considerations, is not required. Again, another explanation of the results may be that some combination of the above two proposals is operative. These alternatives may be tested, and this has been done.

Examination of the phthalate anion will show that if it is involved in a very loose ion pair, and if the ortho-

carboxyl proton is participating to a sufficient extent, then it is feasible that all four oxygens may freely equilibrate rather than just the two of the ester linkage. In a species in which all four oxygens are fully equilibrated, the alkyl oxygen would have a larger supply of ^{18}O to draw upon and this would be reflected in a higher ^{18}O incorporation in the returned ester. Whether or not this has occurred may be determined by an examination of the ^{18}O content of the other product of the reduction, w,w'-dihydroxy-o-xylene (DHX). Comparison of this observed value with the values predicted on the basis of two- and four-oxygen equilibration (Appendix IV) should allow one to decide whether two- or four-oxygen equilibration is actually occurring. Such a determination may indicate if the cis-ion pair is actually looser and/or more ionic than the trans-ion pair.

It was impossible to directly measure the ^{18}O content of the DHX since it decomposed in the glc of the glc - ms system. Similarly, the di-trimethylsilyl derivative was too unstable. Therefore, the ^{18}O content of the decomposition product (produced by flash pyrolysis of DHX in the glc) 1,3-dihydroisobenzofuran (DHIF) was measured instead. If one assumes that there is no kinetic isotope effect involved in the pyrolysis of DHX to DHIF, then a comparison of the observed and predicted values of the ^{18}O content in the DHIF should show whether two- or four-oxygen equilibration has occurred in each case.

This has been done for the DHX produced by both esters

TABLE IX

Predicted and Observed Values for the ^{18}O Content of 1,3-Dihydroisobenzofuran From The Neat Partial Pyrolysis of *cis*- and *trans*-1,2-Dimethylcyclohexyl Hydrogen Phthalate Esters

Sample	Predicted Values		Observed Values
	2-Oxygen Equilibration	4-Oxygen Equilibration	
trans	10.47	10.72	10.55
	10.38	10.66	10.40
	10.29	10.60	10.23
cis	10.42	10.62	10.64
	10.22	10.49	10.52
	10.07	10.39	10.40

(70% pyrolysis), and the results are shown in Table IX and are graphically represented in Figure 11.

As may be seen in Table IX and Figure 11, the results strongly suggest that the intimate ion pair produced in the case of the *cis*-ester allows isotope exchange to occur via a four-oxygen equilibrating mechanism, while in the case of

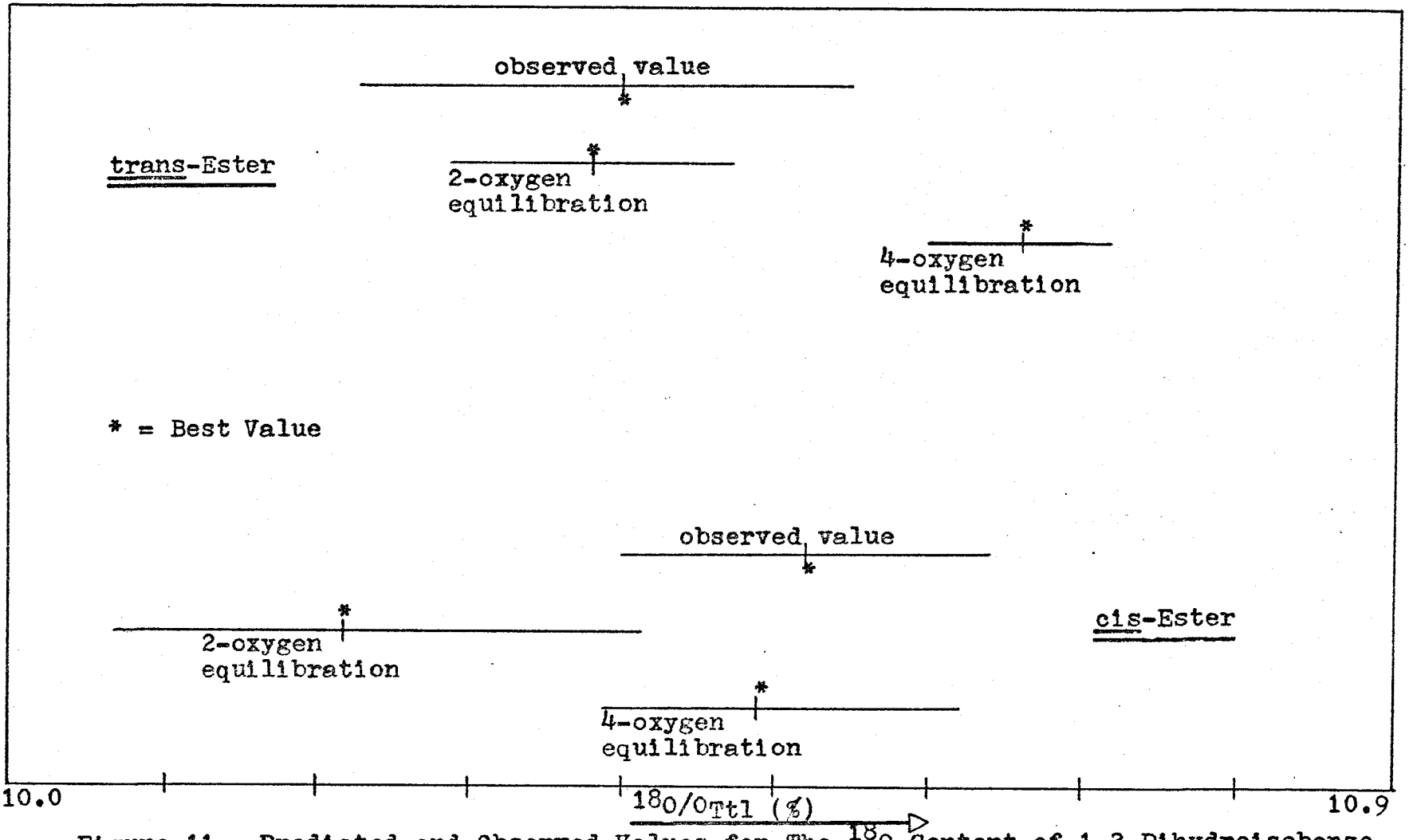


Figure 11 - Predicted and Observed Values for The ^{18}O Content of 1,3-Dihydroisobenzofuran From The Partial Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate Esters in The Neat

the trans-ester the intimate ion pair appears to allow for isotope exchange via a two-oxygen equilibrating mechanism. The implication is obvious. Thus, in agreement with prediction, the cis-intimate ion pair appears to be looser and/or more ionic than the trans-intimate ion pair.

Assuming that the cis-ester ion pair undergoes a process of four-oxygen equilibration while the trans-ester ion pair undergoes a process of two-oxygen equilibration, then the per cent exchange (70% pyrolysis) values are equal to 24.21% for the trans-ester and 19.91% for the cis-ester (Appendix III). These values would appear to negate the suggestion that the cis-ester has undergone the total process of ionization, equilibration, and return to a greater degree than the trans-ester. If such were the case, the relative magnitudes of these numbers would be reversed.

Thus, all the results presently available seem to be best correlated by a mechanism which involves the reversible formation of an intimate ion pair as the rate-determining step. This intermediate appears to be the source of both products and isotope exchange. The cis-intimate ion pair appears to be looser and/or more ionic than the trans-intimate ion pair while the amount of the total process of ionization, equilibration and return to starting material appears to be greater for the trans-than for the cis-ester. If, in either case, solvent-separated ion pairs are formed, their formation would appear to be an essentially irreversible process and a minor contributor in the pyrolysis of these

esters. Thus, these results appear to be compatible with the reaction scheme of Figure 9, where path b is followed preferentially.

Kinetic Studies on the Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate Esters in N,N-Dimethylformamide

As was previously suggested (in the Introduction), it was felt that a detailed investigation into the kinetics of pyrolysis of cis- and trans-1,2-dimethylcyclohexyl hydrogen phthalate esters in solvent would aid in the understanding of the results obtained from the 1-phenyl-2-methylcyclohexyl system. Furthermore, it was hoped that the results from this study would provide a suitable test of the generalized reaction scheme of Figure 9, and allow a deeper understanding of the nature of ester pyrolysis in solution.

N,N-Dimethylformamide (DMF) was chosen as the solvent for these pyrolyses in order that they might be comparable and consistent with the previous studies on the 1-phenyl-2-methylcyclohexyl system.[17] Also, it was hoped that the previously observed virtues of this solvent (solubility of starting material and products, high boiling point, inertness, etc.) would be observed in this system. The experimental technique employed here was essentially the same as that used by Wassenaar for the 1-phenyl-2-methylcyclohexyl system.[17] The results, including first-order rate constants and activation parameters (Appendix I), are listed in Table X.

TABLE X

Kinetic Studies on The Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate Esters in N,N-Dimethylformamide

Compd	Temp °C	Rate Constant k, ($Sec^{-1}x10^6$)	Energy of Activation E_{exp} (Kcal/Mole)	Arrhenius A (Sec^{-1})	Entropy of Activation $\Delta S^{\#}$ (eu)	No of Pts	Percent Complete	Correlation Coefficient
trans	125.0	42.6				25	50	0.9973
	130.0	49.6				31	70	0.9828
	130.0	66.8				25	43	0.9945
	130.0	85.2				20	55	0.9899
	135.0	75.6				27	50	0.9963
	135.0	104.8	24.6 ± 0.6	$13.55x10^9$	-14.8 ± 0.3	24	58	0.9861
	140.0	146.3				25	57	0.9938
	145.0	207.7				30	56	0.9954
	150.0	307.3				30	65	0.9984
	150.0	307.9				18	60	0.9943
cis	125.0	52.5				22	29	0.9958
	130.0	71.3				27	44	0.9852
	135.0	111.2	19.2 ± 0.4	$18.17x10^5$	-32.5 ± 0.3	17	31	0.9954
	140.0	135.3				18	26	0.9944
	145.0	177.6				31	28	0.9931
	150.0	215.7				30	36	0.9960

trans $\Delta G^{\#}$ = 31.4 Kcal/Mole @ 125° cis $\Delta G^{\#}$ = 31.4 Kcal/Mole @ 125°

The temperature range employed here (125-150°) for the pyrolysis of both esters is as large as the technique would allow without introducing serious error. Had the boiling point of the solvent been higher (154°), runs at temperatures higher than 150° might have been feasible. Runs at lower temperatures were impracticably slow.

The rates of pyrolysis of both esters in DMF are much lower than those observed for the corresponding esters in the neat at the same temperature. In the case of the trans-ester, the rate decrease (at 125°) is about tenfold while in the case of the cis-ester, the decrease (at 125°) is about twentyfold. Also, it is notable that in DMF the rate of pyrolysis of the trans-ester is greater than that of the cis-ester at the high end of the temperature range studied and lower at the low end. No such cross-over was observed in the neat pyrolyses, and the cis-ester always pyrolyzed faster than the trans-ester throughout the entire temperature range studied.

Clearly, the solvent has a significant effect on the pyrolysis of these esters. Not only is it exhibiting rate retarding effects in both cases, but also its effect is greatest on the cis-ester. These solvent effects may tell us a great deal about the system under examination. It is well known[21] that a polar solvent will aid reactions involving charge development (in the rate-determining step) through its ability to solvate the charged species. This solvation would be expected to result in a structuring of

solvent and a subsequent loss of freedom of motion. Thus, one should expect that in a reaction involving charge development (in a polar solvent), there should be a lowering of the energy of activation and a subsequent decrease in the entropy of activation. The larger the amount of charge development, the larger these changes should be. These effects are observed in this system and they follow the predicted pattern. The experimental energy of activation for the pyrolysis of the trans-ester in DMF is 26.4 kcal/mole, 6 kcal/mole less than that observed in the neat pyrolysis of this ester. In the case of the pyrolysis of the cis-ester in DMF the experimental activation energy is only 19.2 kcal/mole, 15 kcal/mole less than was observed for the pyrolysis of this ester in the neat. Appropriately, the entropies of activation for the pyrolysis of these esters are much lower than those observed for neat pyrolysis. For the trans-ester the decrease is from 6 eu to -14.8 eu, while for the cis-ester the change is from 10 eu to -32.5 eu. Obviously, the lowering of the experimental energy of activation involves a corresponding lowering of the entropy of activation.

Thus, for both esters, the results indicate a large amount of charge development in the rate-determining step, the amount being greater in the case of the cis-ester. One might have predicted this having seen the results of the study of the neat pyrolysis of these esters. Both the isotope exchange and entropy of activation values indicated that there

was heterolysis occurring in the pyrolysis of both esters. Furthermore, these results indicated that the ion pair formed from the cis-ester was looser and/or more ionic than the ion pair formed from the trans-ester. There is a significant difference here however. In the neat pyrolysis it is felt that in both cases the rate-determining step is the formation of an intimate ion pair. In the pyrolysis in DMF, the large negative entropies of activation indicate a greater decrease in randomness than could be expected from solvation of intimate ion pairs. Therefore, it appears that the rate-determining step for the pyrolysis of either ester in DMF is the formation of a solvent-separated ion pair according to the reaction scheme of Figure 9, where path a and/or c is followed.

Product Distribution Studies on the Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate Esters in N,N-Dimethylformamide

If the formation of a solvent-separated ion pair is the rate-determining step in the pyrolysis of each of these esters, then it is possible that these solvent-separated ion pairs may be the product-determining intermediates. If this is true, then it should be manifested in the product distributions. The anion proximity effects which were so important in determining the product distributions in the neat pyrolyses should now be less important. Furthermore, the solvent-separated ion pairs from these esters should be similar in

character, leading to similar product distributions. Also, since it is well-known that elimination from carbonium ion-like species usually leads to a Saytzeff type product distribution,[22] then the product distributions from these pyrolyses should show a high degree of Saytzeff character.

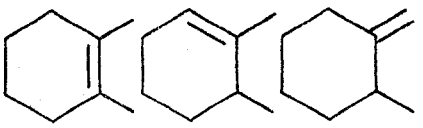
The product distributions have been measured by glc of the residual pyrolysates from the kinetic runs. Any remaining ester was removed so that its pyrolysis in the injection port could not effect the measured product distribution. The results of the product distribution studies on the pyrolysis of both esters are listed in Table XI.

The results are in agreement with the predictions made on the basis of the rate studies. Pyrolysis of both the cis- and trans-esters in DMF produces very similar product distributions, indicating both the relative absence of anion proximity effects and the similarity of the product-determining intermediates. Also, in both cases, the predicted predominance ($\sim$ 50%) of the "extreme" Saytzeff product (1,2-dimethylcyclohexene) is observed. Thus, these results indicate that for both esters the product-determining intermediate is a solvent-separated ion pair. These results provide further support for an ionic mechanism for the pyrolysis of these esters, and are consistent with either path a and/or c (Figure 9).

Kinetic Studies on the Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Methyl Phthalate Diesters in N,N-Dimethylformamide

TABLE XI

Product Distribution Studies on The Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate Esters in N,N-Dimethylformamide

Compound	Temp (°C)	Duration (Min)	Product Distribution (%)		
					
trans	125	300	52.5	26.0	21.5
	130	180	50.5	27.6	21.9
	130	130	53.6	27.1	19.3
	140	84	51.5	25.8	22.7
	145	66	51.4	26.3	22.3
	150	42	52.8	26.4	20.8
	150	55	51.0	27.0	22.0
	Average		51.9	26.6	21.5
cis	130	140	48.6	21.6	29.8
	135	80	48.1	26.9	25.0
	140	34	46.8	22.2	31.0
	145	30	48.7	21.6	29.7
	Average		48.1	23.1	28.8

The above described studies on the pyrolysis of the hydrogen phthalate esters in DMF have indicated that the pyrolysis proceeds via the rate-determining formation of solvent-separated ion pairs. The formation of such ion pairs must require the phthalate moiety to behave as a reasonably good leaving group. In the neat pyrolyses, this leaving group character was found to be enhanced by participation of the ortho-carboxyl proton, and similar behaviour is to be expected in the case of pyrolysis of these esters in DMF. Therefore, a kinetic study of the pyrolysis of cis- and trans-1,2-dimethylcyclohexyl methyl phthalate diesters in DMF was undertaken as a test for such participation.

The technique employed in these studies was the same as that used to follow the pyrolysis of the corresponding hydrogen phthalate esters in DMF with the exception that the esters were added to the hot solvent by syringe since they were viscous liquids rather than solids. Only one run was carried out for each ester, and the temperature used was 150° in both cases. The results are reported in Table XII.

As expected, the methyl phthalate diesters pyrolyzed at lower rates than the corresponding hydrogen phthalate esters. There is approximately a thirtyfold rate decrease in the case of the trans-ester and approximately a tenfold rate decrease in the case of the cis-ester. This indicates that the ortho-carboxyl proton does participate in the rate-

TABLE XII

Kinetic Studies on The Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Methyl Phthalate Diesters in N,N-Dimethylformamide

Compound	Temp (°C)	Rate Constant k^{*} ($sec^{-1}x10^{6}$)	Rate Constant k^{**} ($sec^{-1}x10^{6}$)	Rate Ratio $\frac{k^{**}}{k^{*}}$	Number of Points	Percent Complete	Correlation Coefficient
trans	150.0	9.7 ± 0.2	307.6 ± 40.0	32	23	35.6	0.9965
cis	150.0	22.6 ± 0.5	215.7 ± 19.7	9.5	18	36.8	0.9934

k^{*} = Rate constant for the pyrolysis of the methyl phthalate diester

k^{**} = Rate constant for the pyrolysis of the hydrogen phthalate ester

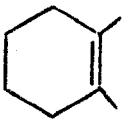
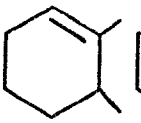
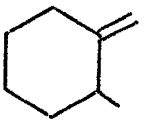
determining step of the pyrolysis of both hydrogen phthalate esters in DMF. The degree of importance of this participation appears to be less for the cis-ester than for the trans-ester. In fact, the cis-methyl phthalate diester pyrolyzes twice as fast as the trans-epimer, whereas the reverse was true in the hydrogen phthalate ester pyrolyses. This may imply a change in the mechanistic character of these pyrolyses such that solvent-separated ion pairs are no longer formed. Alternatively, if such ion pairs are formed, it may mean that the cis-ion pair is more readily solvated than the trans-ion pair thus diminishing its relative dependence on ortho-carboxyl proton enhancement of leaving group ability. In any case, the importance of the ortho-carboxyl proton is demonstrated, and once again supports the postulate of Wassenaar.[17] Furthermore, the existence of such participation is in itself evidence for an ionic type mechanism in the pyrolysis of these esters.

Product Distribution Studies on the Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Methyl Phthalate Diesters in N,N-Dimethylformamide

As in the case of the pyrolysis of the methyl phthalate diesters in the neat, any change in the character of the product-determining intermediate should manifest itself in the product distributions. Accordingly, the products from these pyrolyses were analyzed in the same manner as was used for the hydrogen phthalate ester pyrolyses (in DMF).

TABLE XIII

Product Distribution Studies on The Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Methyl Phthalate Diesters in N,N-Dimethylformamide

Compound	Temp (°C)	Duration (Min)	Product Distribution (%)		
					
trans	150.0	720	4.1	36.2	59.7
cis	150.0	315	22.1	22.9	55.0

The only exception was that the olefins and DMF were separated from nonvolatile products by trap to trap distillation. The results are shown in Table XIII.

A comparison of these product distributions with those from the pyrolysis of the corresponding hydrogen phthalate esters (Table XI) shows a large difference between the two. Furthermore, the cis- and trans-diesters do not produce similar product distributions, indicating that the product-determining intermediates from them are dissimilar in character and therefore, cannot be solvent-separated ion pairs. This is supported by the fact that there is very

little extreme Saytzeff product produced particularly by the trans-ester. In fact, the product distributions which result from the pyrolysis of these diesters in DMF are very similar to those obtained from the gas phase pyrolysis of cis- and trans-1,2-dimethylcyclohexyl acetate.[14] This is significant since it implies a similarity in character of the pyrolysis of the acetate and methyl phthalate diesters of these alcohols. If this is true, then these pyrolyses may have similar product-determining intermediates which could not be solvent-separated ion pairs and which would have to be either intimate ion pairs or covalent species. In the case of the methyl phthalate diesters, the product-determining intermediate appears to be a relatively tight, intimate ion pair since the pyrolysis of the trans-ester leads to formation of 4% of the 1,2-dimethylcyclohexene.

Whatever the product-determining intermediate, the very large difference in the product distributions from both the cis- and the trans-methyl phthalate diesters as compared to those from the hydrogen phthalate esters confirms the importance of the participation of the ortho-carboxyl proton in the product-determining step of hydrogen phthalate ester pyrolysis. The fact that this participation does occur both in the rate-determining and product-determining steps of these pyrolyses once again supports an ionic mechanism for the pyrolysis of these esters.

Isotope Exchange Studies on the Partial Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate Esters in N,N-Dimethylformamide

The above discussed kinetic and product distribution studies on the pyrolysis of both the hydrogen phthalate esters and the methyl phthalate diesters in DMF have indicated that an ionic mechanism is realistic for the former. If, as expected, this mechanism involves the reversible formation of ion pairs, then isotope exchange should be observable as it was in the neat pyrolyses.

As in the case of the neat isotope exchange studies, both esters were synthesized with 11 atom per cent ^{18}O at each oxygen except the ester alkyl oxygen which contained only the natural abundance (0.20%) of ^{18}O. These esters were then partially pyrolyzed under exactly the same conditions as were used for the kinetic studies, for lengths of time calculated to result in 0, 20 and 70% decomposition. The unpyrolyzed esters were recovered, purified and reduced to the 1,2-dimethylcyclohexanols and DHX. These products were separated and the 1,2-dimethylcyclohexanols were analyzed by glc for geometrical isomerization and by mass spectrometry for ^{18}O content. The DHX was handled in the manner previously described and the DHIF produced was analyzed for ^{18}O content by mass spectrometry. The results of the analyses for geometrical isomerization are listed in Table XIV. The results of the analyses for ^{18}O content in

TABLE XIV

Geometrical Isomerization in the Partial Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate Esters in N,N-Dimethylformamide

Compound	Temp (°C)	Duration (min)	Per Cent Decomposition	Per Cent Isomerization
trans	-	-	0.0	0.0
	125.0	86.5	20.0	0.0
	125.0	471.2	70.0	0.0
cis	-	-	0.0	0.0
	125.0	70.0	20.0	0.0
	125.0	383.2	70.0	0.0

the alcohol and DHIF are listed in Tables XV and XVI respectively.

The fact that no geometrical isomerization was observed under the range of conditions studied may be interpreted in several ways. It may simply mean that a solvent-separated ion pair is not generated. Alternatively, if a solvent-separated ion pair is generated, it may be configurationally

stable so that return results in no isomerization or, finally, there may merely be no return from solvent-separated ion pair to starting material. The first of these suggestions contradicts the conclusions drawn on the basis of the kinetic and product distribution studies. The second of these explanations seems improbable since a solvent-separated ion pair should be sufficiently loose to allow for at least some return (of the anion) to the opposite side of the cyclohexyl moiety from which it left.[20] Therefore, it appears that in the pyrolysis of both of these esters in DMF, the formation of solvent separated ion pairs is an essentially irreversible process. This would mean that if any isotope exchange is observed in the partial pyrolysis of the labelled esters, it must be a result of scrambling of the oxygen atoms in reversibly formed intimate ion pairs. Isotope exchange is observed as is shown in Table XV. Again, the values from the 0% decomposition studies serve to show that the method of pyrolysis and work-up does not introduce any extraneous ^{18}O incorporation. The values of ^{18}O exchange at 20 and 70% decomposition show that time dependent ^{18}O exchange does occur in the pyrolysis of both esters. Therefore, it appears that as stated above, there is reversible formation of intimate ion pairs involved in the pyrolysis of both the cis- and the trans-esters in DMF.

Further interpretation of these results is possible. In the studies involving 20 and 70% decomposition, the trans-ester shows more ^{18}O incorporation than the cis-ester. This is opposite to what was observed in the neat pyrolyses. Since it

TABLE XV

^{18}O Incorporation in The Partial Pyrolysis of *cis*- and *trans*-1,2-Dimethylcyclohexyl Hydrogen Phthalate Esters in N,N-Dimethylformamide

Compound	Temp (°C)	Duration (Min)	Percent Decomp	M+2/M (%)	$^{18}O/O_{Ttl}$ (%)	Percent Exchange
trans	-	-	0.0	.590	.233	0.0
	125.0	86.5	20.0	.909 .754 .605	.553 .398 .250	3.06*
	125.0	471.2	70.0	1.750 1.605 1.516	1.377 1.235 1.148	18.56*
cis	-	-	0.0	.570	.215	0.0
	125.0	70.0	20.0	.875 .650 .464	.518 .294 .200	1.46* .97**
	125.0	382.3	70.0	1.566 1.415 1.312	1.196 1.050 .953	15.44* 10.29**

* based on "two-oxygen equilibration" ** based on "four-oxygen equilibration"

is felt that in both the neat and the DMF pyrolyses, exchange occurs within intimate ion pairs, it appears that there may be a character reversal (in the intimate ion pairs) in going from the neat to DMF. This is unexpected and is not necessarily true. As was pointed out in the discussion of the isotope exchange studies from the neat pyrolyses, there may be several sources of these differences in the amount of ^{18}O incorporated in the cis- and the trans-esters. The same three alternatives apply here, and they may be tested in a similar manner. This has been done and the results comparing predicted and observed values for the ^{18}O content of the DHIF from the cis and the trans-esters are reported in Table XVI and are graphically represented in Figure 12.

The results are most easily seen in Figure 12 where the best values and the errors are put in perspective. It is immediately obvious that these results are not near as conclusive as those obtained from the neat pyrolyses. The error limits on the observed values are quite large, and there is considerable overlap on both sets of values for the cis-ester. The results are still indicative however, and the "best" values do indicate that as in the neat pyrolyses, exchange occurs through a two-oxygen equilibrating intermediate in the case of the trans-ester, and a four-oxygen equilibrating intermediate in the case of the cis-ester. Therefore, it appears that the cis-intimate ion pair is looser and/or more ionic than that of the trans-ester.

TABLE XVI

Predicted and Observed Values for the ^{18}O Content of 1,3-Dihydroisobenzofuran From the Partial Pyrolysis of *cis*- and *trans*-1,2-Dimethylcyclohexyl Hydrogen Phthalate Esters in N,N-Dimethylformamide

Sample	Predicted Values		Observed Values
	2-Oxygen Equilibration	4-Oxygen Equilibration	
trans	10.57	10.79	10.68
	10.53	10.76	10.46
	10.46	10.72	10.23
cis	10.66	10.79	10.98
	10.61	10.75	10.76
	10.54	10.70	10.56

As in the case of the neat pyrolyses, the per cent exchange values may be used to gauge the rapidity of the total process of ionization, exchange and return to covalent starting material. Assuming that the exchange occurs as outlined above, the per cent exchange (during 70% pyrolysis) is 18.56% for the *trans*-ester and 10.29% for the *cis*-ester.

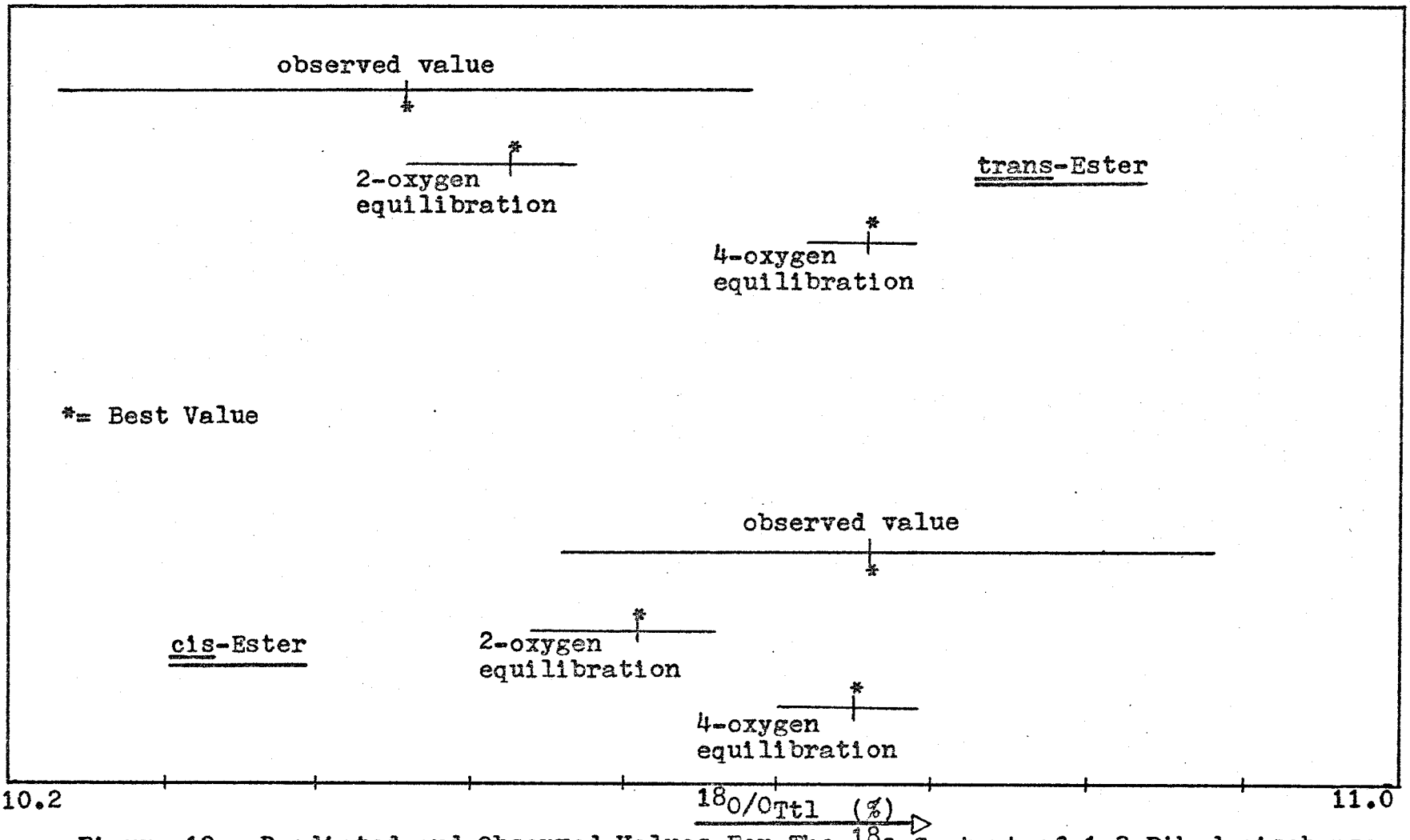


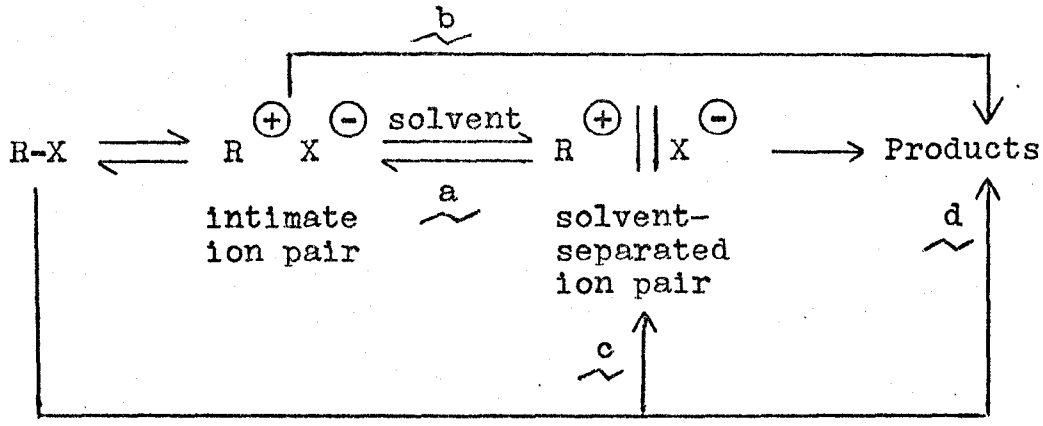
Figure 12 - Predicted and Observed Values For The ^{18}O Content of 1,3-Dihydroisobenzofuran From The Partial Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate Esters in N,N-Dimethylformamide

Conversion of these values to rate constants leads to values of 73 sec^{-1} x 10^{-7} for the trans-ester and 47 sec^{-1} x 10^{-7} for the cis-ester. These exchange values and rate constants for exchange indicate that the process of ionization, exchange and return occurs more rapidly for the trans-ester than for the cis-ester, and this is probably the reason why the trans-ester incorporates more ^{18}O than the cis-ester during the partial pyrolyses.

Considered together, these results indicate that pyrolysis of cis- and trans-1,2-dimethylcyclohexyl hydrogen phthalate esters in DMF occurs primarily via path a (Figure 9). Thus, for both esters there is reversible formation of an intimate ion pair which is looser and/or more ionic in the case of the cis-ester, but more rapidly formed and returned in the case of the trans-ester. This is followed by the rate-determining and essentially irreversible formation of a solvent separated ion pair which is similar in character for both esters and which is the product-determining intermediate in their pyrolysis.

SUMMARY AND CONCLUSIONS

The following general reaction scheme has been proposed for unimolecular pyrolytic elimination reactions.



This scheme has been tested and found capable of rationalizing the behaviour observed in the pyrolysis of cis- and trans-1,2-dimethylcyclohexyl hydrogen phthalate esters both in the neat where path b appears to be followed, and in solvent (DMF) where path a appears to be followed.

Thus, in the neat pyrolysis of each ester, adherence to the first-order rate law indicates unimolecular decomposition of the ester, while the entropy of activation (+6 ± 4 for the trans-ester, +10 ± 1 for the cis-ester) indicates that the heterolysis to form the intimate ion pair is the rate-determining step.[17] The formation of these ion pairs appears to involve some form of participation of the ortho-carboxyl proton since the rate of pyrolysis of these esters is greatly decreased (~ 300-fold) by replacement of this proton with a methyl group. The observation of isotope exchange in the partial pyrolysis of these esters further indicates that ion pairs are formed and shows that this formation is a reversible process. Once formed, the intimate ion pairs from the cis- and trans-esters do not appear to be

identical in character. In fact, the cis-species appears to be looser and/or more ionic than the trans-species. This is first indicated by the entropies of activation whereby the cis-ester shows a greater increase in randomness than does the trans-ester.[17] This is also indicated by the fact that the cis-ester incorporates more ^{18}O than the trans-ester (1.83 vs 1.54 atom % at 70% decomposition). The best evidence for this comes from the observation that the cis-intimate ion pair allows all four oxygens of the phthalate moiety to freely equilibrate while the trans-intimate ion pair allows only the two oxygens of the ester linkage to equilibrate. Finally, this suggestion is supported by the nonidentical character of the olefinic product distributions.[17] Following the intimate ion pairs, it appears that there is little or no reversible formation of solvent-separated ion pairs. This is indicated by the relative absence of the geometrical isomerization that would be expected to result from the reversible formation of such ion pairs. Also, once again, the olefinic product distributions are not consistent with what would be expected for elimination from solvent-separated ion pairs.[17] Thus, the intimate ion pair (from each ester) appears to be the product-determining intermediate. The formation of products appears to result from kinetically controlled (as shown by the absence of olefin equilibration under the pyrolysis conditions) elimination from the intimate ion pair where, in each case, the proximity of the anion to the protons to be removed (of the cation) determines the

relative distribution of olefins. Also, it appears that the ortho-carboxyl proton participates in the product-determining step as shown by the change in the product distribution when the proton is replaced by a methyl group. In conclusion, pyrolysis primarily via path b appears to be most consistent with these results.

The pyrolysis of these esters in DMF produces similar, but not identical, results. Unimolecular decomposition is again observed while the large negative entropies of activation (-14.8 for the trans-ester, -32.5 for the cis-ester) indicate that the formation of solvent-separated ion pairs is the rate-determining step rather than the formation of intimate ion pairs. The reversible formation of the latter type of ion pair does, however, occur. This is shown by the observation of isotope exchange in the partial pyrolysis of both esters. As before, the cis-intimate ion pair appears to be looser and/or more ionic than its trans-epimer. This is indicated by the observation that the cis-intimate ion pair appears to allow free equilibration of all four oxygens of the phthalate moiety while the trans-intimate ion pair appears to allow only the two oxygens of the ester linkage to freely equilibrate. For both esters, the intimate ion pair appears to be directly followed by the rate-determining (as indicated by the entropies of activation) formation of a solvent-separated ion pair. The formation of this ion pair involves some participation of the ortho-carboxyl proton as shown by the decrease in the rate of pyrolysis (30-fold for the trans-

ester and 10-fold for the cis-ester) observed when the proton is replaced by a methyl group. Once formed, this ion pair does not return to starting material as shown by the absence of any geometrical isomerization. Instead, kinetically controlled elimination (there is no olefin equilibration under the pyrolysis conditions) occurs from this intermediate to produce products. This is supported by the fact that (as would be expected for elimination from the cis- and trans-solvent-separated ion pairs) the olefinic product distributions are very similar, and the Saytzeff olefins are formed in the major amount. Once again it appears that the ortho-carboxyl proton participates in this product-determining step as shown by the large shift in the product distributions (from Saytzeff-like to Hofmann-like) when the proton is replaced by a methyl group. Thus, pyrolysis primarily via path a appears to be most consistent with these results.

In final conclusion, the behaviour observed in the pyrolysis of these esters both in the neat and in DMF is similar to that observed in the 1-phenyl-2-methylcyclohexyl system, and all results are consistent with the proposed general reaction scheme for pyrolytic eliminations.

CHAPTER III

EXPERIMENTAL

Infra-red spectra were obtained using Beckman IR-10 and IR-12 spectrophotometers equipped with potassium bromide cells. All solutions were approximately 10 weight-weight per cent in the solvent specified. Absorptions are recorded in reciprocal centimeters (cm^{-1}) and only the significant absorptions are recorded. The intensities are expressed as weak (w, 100-75% transmission) medium (m, 74-40% transmission) or strong (s, 39-0% transmission). All nuclear magnetic resonance spectra were obtained using Jeolco C-60 and C-60HL instruments, and the chemical shifts are expressed in γ units downfield from internal tetramethylsilane. The splitting pattern of each resonance is recorded using the following code: s = singlet, d = doublet, t = triplet, and m = multiplet. All solutions were weight-volume per cent in the solvent specified. All melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. All gas-liquid chromatography (glc) was performed on an F&M model 720 gas chromatograph under the following conditions: injector - 300°, detector - 300°, bridge - 100 mA, helium flow - 1 cc/sec and oven temperature as specified. The columns used are listed below.

TABLE XVII

COLUMNS USED FOR GAS-LIQUID CHROMATOGRAPHY

Column	Length (Ft)	Diameter (In)	Substrate
a	6	1/4	10% PEG 20M
b	8	1/2	10% PEG 20M
c	16	1/4	10% Diisodecyl Phthalate
d	6	1/4	10% SE 30
e	10	1/4	10% DEGS

Peak areas were determined with a disc integrator.

Unless otherwise specified, all reactions were carried out in flame dried flasks using an inert atmosphere (N_2). All solutions were dried by the use of anhydrous magnesium sulfate. All solutions were concentrated *in vacuo*. All distillations were carried out using a vacuum jacketed 10 cm Vigreux column. All temperatures are recorded in degrees Centigrade and all pressures are recorded in millimeters of mercury.

cis- and *trans*-1,2-Dimethylcyclohexanol

The procedure employed here was identical to that used by Wassenaar.[17] Thus, the reaction of 0.25 mole of methylmagnesium iodide with an equivalent amount of 2-methylcyclo-

hexanone yielded after work-up, 27 g (83%) of a mixture of cis- and trans- 1,2-dimethylcyclohexanol in an 18:82 ratio (column a, 120°). All physical and spectral data for this mixture agreed with the literature.[17] This mixture was separated into pure cis- and pure trans-1,2-dimethylcyclohexanol by preparative glc (column b, 120°). Analysis (column a, 120°) of the alcohols obtained in this manner showed each to be pure and free from its epimer. All physical and spectral data for each alcohol agreed with the literature.[17]

Hydrogen Phthalate Esters of cis- and trans-1,2-Dimethylcyclohexanol

The method of Rutherford et al.[23] was employed to convert cis- and trans-1,2-dimethylcyclohexanol to their corresponding hydrogen phthalate esters. The cis-ester was prepared in 55% yield and all physical constants and spectral data are in agreement with the literature.[17] The trans-ester was prepared in 50% yield and all physical and spectral data agreed with the literature[17] with the exception of the melting point which was found to be 130-131° as opposed to the literature value of 125-127°. The esters were examined by ir and nmr spectra, by thin layer chromatography (tlc) (benzene on silica gel), and by glc (column a, 120°) of the alcohols produced when the esters were reduced using lithium aluminum hydride (LAH), and found to be pure.

trans-1,2-Dimethylcyclohexyl Methyl Phthalate Diester

This diester was prepared from the corresponding hydrogen phthalate by the addition of an excess of an ethereal solution of diazomethane[24] to a solution of the hydrogen phthalate ester (2 g, 7.0 mmole) in 10 ml of ether. This yielded 2.1 g (100%) of trans-1,2-dimethylcyclohexyl methyl phthalate: bp 95-100° (0.01 mm); nmr (CCl_4) 2.3-2.8 (m, 4, Ar$\underline{H}$), 6.2 (s, 3, O-C$\underline{H}_3$), 7.0-7.3 (m, 1, C$\underline{H}$), 8.4 (s, 3, C-C$\underline{H}_3$), 8.2-8.8 (m, 8, (C$\underline{H}_2$)$_4$), 9.0-9.1 (m, 3, CH-C$\underline{H}_3$); ir (CCl_4) 3100-3000 (w, ArH), 2980-2860 (s, aliph C-H), 1735 (s, C=O), 1600 (m, Ar), 1580 (m, Ar), 1450 (m, Ar), 1300-1250 (s, C-O), 1140-1080 (s, C-O), 860 (s).

Anal. Calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.24; H, 7.49.

cis-1,2-Dimethylcyclohexyl Methyl Phthalate Diester

This ester was prepared in exactly the same manner as the trans-ester above, yielding 2.1 g (100%) of cis-1,2-dimethylcyclohexyl methyl phthalate diester: bp 95-100° (0.01 mm); nmr (CCl_4) 2.2-2.7 (m, 4, Ar$\underline{H}$), 6.1 (s, 3, O-C$\underline{H}_3$), 7.4-8.9 (m, 9, (C$\underline{H}_2$)$_4$-C$\underline{H}$), 8.5 (s, 3, C-C$\underline{H}_3$), 9.1-9.2 (d, 3, $\underline{J}$ = 7 Hz, CH-C$\underline{H}_3$); ir (CCl_4) 3100-3000 (w, ArH), 2980-2860 (s, aliph C-H), 1735 (s, C=O), 1600 (m, Ar), 1580 (m, Ar), 1450 (m, Ar), 1300-1250 (s, C-O), 1140-1080 (s, C-O), 860 (w).

Anal. Calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.31; H, 7.56.

^{18}O Labelled cis- and trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate Esters

A ^{18}O Labelled Phthalic Acid

Phthalic anhydride (13.7 g, 0.09 mole) dissolved in 50 ml of dry[25] tetrahydrofuran (THF) was placed in a 100 ml, three-necked, round bottomed flask fitted with a magnetic stirrer and a reflux condenser (nitrogen inlet attached). Water (4.9 g, 0.27 mole, 20 atom per cent ^{18}O, Low D, supplier -- Bio-Rad Laboratories) was added, and the solution was stirred at reflux for 20 hr. The solution was cooled to 25°, dry hydrochloric acid was bubbled into it for a period of 30 sec, and the solution was refluxed for 12 hr. The solution was then cooled to 25°, dry hydrochloric acid was bubbled in for 5 min, and the solution was then refluxed for 24 hr. After cooling to 25°, dry hydrochloric acid was again bubbled into the solution. A further hour of stirring at 25° was followed by addition of 250 ml of cold (0°) pentane. The fine white precipitate which resulted was recovered by filtration and washed with 200 ml of hot (60°) chloroform to remove any unreacted phthalic anhydride. This yielded 13.7 g (89%) of phthalic acid: mp 206° d. Examination of this material by tlc (chloroform on alumina) showed it to be pure phthalic acid with no phthalic anhydride present.

B ^{18}O Labelled Phthalic Anhydride

The ^{18}O labelled phthalic acid produced above was converted to the pure anhydride by a combined process of dehydration and sublimation. The ^{18}O labelled phthalic acid (13.7 g, 0.08 mole) was spread evenly in the bottom of a macrosublimator (100 mm OD, cold finger 80 mm OD, mean free path 20 mm), and a vacuum (12.5 cm) was applied. With the cold finger at 25°, the sublimator was slowly heated to 228° in an oil bath and held at that temperature for 4 hr. The fine, white, crystalline solid that formed on the cold finger was removed by scraping and yielded 10.8 g (91%) of phthalic anhydride: mp 131.5-133.5°. The physical properties and spectral data of the product agreed with those of authentic phthalic anhydride. Mass spectral analysis indicated 11.03 atom per cent ^{18}O at each oxygen atom in the compound.

^{18}O Labelled *cis*- and *trans*-1,2-Dimethylcyclohexyl Hydrogen Phthalate Esters

The procedure of Rutherford *et al.*[23] was again employed. The reaction of *trans*-1,2-dimethylcyclohexanol (3.0 g, 0.0235 mole) with ^{18}O labelled phthalic anhydride (3.48 g, 0.0235 mole) yielded 4.1 g (63%) of the ^{18}O labelled *trans*-1,2-dimethylcyclohexyl hydrogen phthalate ester. All spectral and physical properties were in agreement with those previously reported for the ^{16}O ester. The reaction

of cis-1,2-dimethylcyclohexanol (3.0 g, 0.0235 mole) with ^{18}O labelled phthalic anhydride (3.48 g, 0.0235 mole) yielded 4.9 g (75%) of the cis-1,2-dimethylcyclohexyl hydrogen phthalate ester. All physical and spectral data were in agreement with those previously reported for the ^{16}O ester.

Kinetic Studies on the Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate Esters in N,N-Dimethylformamide

Thirty-five ml of N,N-dimethylformamide (DMF) purified according to the method of Vogel[25] was pipetted into a 100 ml, three-necked, round-bottomed flask which was fitted with a mechanical stirrer, a condenser, and a septum with a hypodermic syringe. The apparatus was immersed in a Haake NBS Circulator maintained at the desired temperature ($\pm < 0.1^{\circ}$), and equilibrated for 1 hr. The condenser was removed momentarily and an accurately weighed pellet of the ester (0.5-0.6 g) was introduced into the flask. After an initial waiting period to ensure complete dissolution of the ester (1-2 min), 1 ml samples of the pyrolysate were removed at set intervals and injected into separate 25 ml Erlenmeyer flasks containing 5 ml of cold (0°) THF. The samples were titrated with standard base against phenolthalein indicator. Appropriate solvent blank titrations were made, and the base was standardized against potassium acid phthalate in water

before and after each kinetic run. Expansion of the DMF during the process of heating from room temperature to the pyrolysis temperature was accounted for by the use of a dilatometer containing DMF.

All calculations other than standardization of base and correction of solvent volume for expansion were carried out by use of an IBM 360-50 computer using the program reproduced in Appendix I. Complete explanations of the calculations of initial ester concentration, ester concentration at time zero, ester concentration at any time (t), rate constants (and errors in rate constants) and activation parameters (and errors in activation parameters) are contained in the comment cards (C) in the computer program. A brief, simplified explanation of some of these calculations follows.

The actual ester concentration at time zero is a necessary value for all further calculations, and is not the concentration which would be calculated on the basis of weight of ester added and corrected solvent volume. This is due to the fact that some of the ester must have pyrolyzed during the waiting period for complete dissolution. The ester concentration at time zero may be calculated in the following manner. (Note that all terms defined here are as defined in the computer program)

A Calculation of Initial Ester Concentration

Let: ESCONC = the calculated ester concentration at t = 0 considering that during dissolution some ester must have pyrolyzed.

WTSAMP = the weight of ester added.

MW = the molecular weight of the ester.

VSOLV = the volume of solvent (corrected for expansion).

TERM1 = the theoretical concentration of the ester in the reaction mixture considering only measured weight and calculated volume.

Then: TERM1=(WTSAMPx1000)/(MWxVSOLV)

Now let: VEXPTL(1) = the volume of base necessary to titrate the aliquot taken at t = 0.

VEXPTL(I) = the volume of base necessary to titrate an aliquot taken at any time (t).

VBLANK = the amount of base necessary to titrate the solvent blank.

BASEN = the normality of the base used for the titrations.

Then: ESCONC=TERM1-((((VEXPTL(1)-VBLANK)BASEN)-TERM1)/2)

Thus, the ester concentration at t = 0 (ESCONC) is equal to the starting ester concentration (TERM1) minus the number of moles of ester pyrolyzed during dissolution. The second term on the right hand side (RHS) is divided by two since a dibasic acid is generated and we are working in moles.

B Calculation of Ester Concentration at Any Time (t)

Having calculated the initial concentration of the ester at t = 0 (ESCONC), this value must be used to calculate the amount of ester left at any time (t) which is necessary for substitution in the first-order rate equation. These values may be calculated in the following manner.

Let: VBASE(1) = the volume of base necessary to titrate the ester only at t = 0.

VCORR = the volume of base necessary to titrate the solvent blank plus the acid generated by pyrolysis during dissolution.

ALIQOT = the volume of the sample of the pyrolysate at any time (t).

ESLEFT = the amount of ester left at any time (t)

Then: VBASE(1) = ESCONC/BASEN

VCORR = VEXPTL(1)-VBASE(1)

VBASE(I) = VEXPTL(I)-VCORR

∴ ESLEFT(I)=(2xESCONCxALIQOT/1000)-(BASENxVBASE(I)/1000)

In practical terms, the first term on the RHS represents the maximum number of equivalents of acid that could be generated in the aliquot if complete pyrolysis of the ester were to occur. The second term on the RHS is the sum of the number of equivalents of acid formed plus the number of equivalents of ester left in the aliquot. Since one equivalent of ester, when pyrolyzed, forms two equivalents of acid, then the difference in these two terms must be equal to the number of equivalents of ester in the aliquot.

C Calculation of Rate Constants

The rate constant was calculated using the first order rate equation,

$$\ln E_L = - kt + \ln E_o$$

where: E_L = ester left at any time (t)

E_o = ester left at time t = 0

k = rate constant (sec^{-1})

t = time (sec)

The line of best fit was found by use of the least mean squares subroutine (LMS) in the computer program (Appendix I).

D Calculation of Activation Parameters

The frequency factor and experimental energy of activation were calculated from the Arrhenius equation,

$$k = Ae^{-E_{exp}/RT}$$

in the form

$$\ln k = - E_{exp}/RT + \ln A^{26}$$

where: k = rate constant (sec^{-1})

E_{exp} = experimental energy of activation (cal $mole^{-1}$)

R = gas constant (cal deg^{-1} $mole^{-1}$)

T = absolute temperature (deg)

A = frequency factor (sec^{-1})

The quantity E_{exp} is equal to the slope of the line resulting from a plot of ln k against 1/RT where ln A is

found from the intercept on the y axis. Again, the line of best fit was determined by use of the LMS subroutine.

A combination of the absolute rate equation:

$$k = Ke(k'T/h)e^{\Delta S^{\#}/R}e^{-E_{exp}/RT}$$ [27]

with the Arrhenius equation:

$$k = Ae^{-E_{exp}/RT}$$

yields, upon rearrangement

$$\Delta S^{\#} = R \ln (h/e\,k'\,T) + R \ln A$$

where: k, E_{exp}, R, T and A are as previously defined.

K = transmission coefficient, considered to be unity.

k' = Boltzmann constant (erg deg^{-1} $molecule^{-1}$)

h = Planck constant (erg sec $molecule^{-1}$)

$\Delta S^{\#}$ = entropy of activation (cal deg^{-1} $mole^{-1}$)

As before, ln A is the intercept on the y axis.

Determination of Rate Constants for the Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Methyl Phthalate Diesters in N,N-Dimethylformamide

These kinetic runs were handled in a very similar manner to those of the hydrogen phthalate esters in DMF. The only change in procedure involved the addition of the

viscous diesters to the hot solvent by means of a syringe which was weighed before and after the addition. The frequency with which samples were to be taken and titrated was predetermined by following a simulated kinetic run by tlc (ether on alumina). Also, since the starting material contained no acidic function and the product was only a monobasic acid, the calculations were of necessity altered in the following manner.

Now: ESCONC=TERM1-((VEXPTL(1)-VBLANK)BASEN)

where all terms are as previously defined. In the above equation, the actual ester concentration (ESCONC) is determined by subtracting the number of acid equivalents from the theoretical ester concentration. We need no longer divide by two since only a monobasic acid is generated, and we need no longer subtract the theoretical ester concentration (TERM1) since the ester itself has no acidic function.

Similarly, the calculation of the amount of ester left at any time (t) must be changed. Thus, the equations used are altered in the following manner.

VCORR = VEXPTL(1)

This is a result of the fact that any acid present must be a result of pyrolysis during dissolution.

ESLEFT(I)=(ESCONCxALIQOT/1000)-(BASENxVBASE(I)/1000)

where all terms are as previously defined. This equation differs from that used for the hydrogen phthalate esters in that the first term on the RHS is no longer doubled since pyrolysis of the ester generates only a monobasic acid and

the starting ester contains no acidic function. Similarly, the second term on the RHS is equal to only the moles of acid generated during pyrolysis. Therefore, the above equation simply states that the moles of ester left at any time (t) (ESLEFT(I)) is equal to the starting moles of ester (ESCONC) in the aliquot minus the moles of acid generated. These modified equations are employed to obtain values of ln ester left versus time for substitution in the first-order rate equation as previously described.

Determination of Rate Constants for the Neat Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Methyl Phthalate Diesters

The experimental technique of neat pyrolysis is quite different from that of solvent pyrolysis. This technique has been described by Wassenaar[17] for the neat pyrolysis of cis- and trans-1,2-dimethylcyclohexyl hydrogen phthalate esters, and the technique employed here was identical with but one exception. The frequency with which samples were to be taken was predetermined by following a simulated kinetic run using tlc (ether on alumina). As in the case of the pyrolyses in solvent, all calculations except the standardization of the base were carried out by an IBM 360-50 computer using the program reproduced in Appendix I.

A brief, simplified explanation of the calculations (as they differed from those previously described) follows.

A Calculation of Initial Ester Concentration

Let: TERM1 = the theoretical number of equivalents of ester in each test tube, considering only the weight of the ester and its molecular weight.

WTSAMP = the weight of the ester in each test tube.

MW = the molecular weight of the ester.

Then: TERM1=WTSAMP/MW

Now let: VEXPTL(1) = the volume of base necessary to titrate the sample at t = 0.

VBLANK = the volume of base necessary to titrate the solvent blank.

BASEN = the normality of the base used for the titrations.

ESCONC = the actual moles of ester at t = 0, considering that during the warm-up period, some of the ester must have pyrolyzed.

Then: ESCONC=TERM1-((VEXPTL(1)-VBLANK)BASEN)

Thus, the actual number of moles of ester at t = 0 (ESCONC) is equal to the calculated moles of ester (TERM1) minus the

number of moles of acid generated.

B Calculation of First-Order Rate Constants

In order to calculate the desired first order rate constant for the pyrolysis, the values of ln ester left at various times (t) must be determined. This was done in the following manner.

Let: VCORR = the volume of base necessary to titrate the solvent blank plus any acid generated by pyrolysis during warm-up.

VEXPTL(I) = the volume of base necessary to titrate a sample taken at any time (t).

ESLEFT(I) = the amount of ester left at any time (t).

Then: VCORR=VEXPTL(1)

VBASE(I)=VEXPTL(I)-VCORR

and ∴ ESLEFT(I)=ESCONC-(BASENxVBASE(I)/1000)

Thus, the moles of ester left at any time (t) (ESLEFT(I)) is equal to the initial moles of ester present (ESCONC) minus the moles of acid produced. From the above equation, values of moles of ester left versus time may be obtained for sub-

stitution in the first-order rate equation and the rate constant may be obtained in the manner previously described.

Determination of Olefinic Product Distributions

Method 1 -- Pyrolysis of *cis*- and *trans*-1,2-Dimethylcyclohexyl Hydrogen Phthalate Esters in N,N-Dimethylformamide

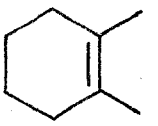
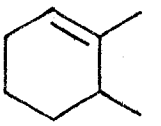
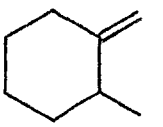
In these cases, the distribution of olefins in the residual pyrolysate from each kinetic run was determined. The remaining pyrolysate (usually about 5-6 ml) was added to 30 ml of sodium hydroxide (0.1 N), and extracted twice with 5 ml portions of pentane. The pentane layer was washed twice with 5 ml portions of water, dried and concentrated to a volume of about 1 ml. Samples of the concentrate were analyzed by glc (column c, 70°) and the relative amount of each olefin was determined by integration of the glc trace. The results are listed in Table XI.

This procedure was checked to ensure that it yielded the correct olefin distributions. A standard solution containing 0.1 g of olefins of a known distribution (Table XVIII, sample 1), hydrogen phthalate ester (0.25 g), and phthalic acid (0.15 g) in 35 ml of DMF was analyzed using the above procedure. A total of seven analyses encompassing a period of four weeks were carried out and the method was found to give consistent, acceptable results.

The distribution of the product olefins was also shown to be inert to the pyrolysis conditions by the following

TABLE XVIII

Distributions of Olefins Used in Standard Solutions

Sample	Olefin Distribution %		
			
1	43.2	51.7	5.1
2	19.5	50.5	29.8

procedure. A solution of 0.07 g of olefins of a known distribution (Table XVIII, sample 2) in 10 ml of DMF containing 0.12 g of phthalic acid was stirred at 150° for a period of 2 hr. The resultant solution was worked up by the above described method and the distribution of olefins was measured. There was no detectable change in the olefinic product distribution.

Method 2 -- Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Methyl Phthalate Diesters in N,N-Dimethylformamide

As in the case of the hydrogen phthalate esters, the product distributions were determined from the residual pyrolysates of each kinetic run. However, since any unpyrolyzed starting ester could not be removed from the residue by the extraction procedures employed in method 1, the olefins and DMF were separated from the residue by trap to trap distillation (0.01 mm, pot 45°, trap-196°, mean free path 34 cm). Virtually all the liquid distilled after 4 hr, but the system was set to run a minimum of 24 hr in order to ensure complete transfer of all olefins. The resultant solution was subjected to the same work-up as in method 1 with the exception that water was used in place of the sodium hydroxide solution. The results are listed in Table XIII. Also, it was shown in a similar manner to that used in method 1 that this method yielded the correct olefin distributions.

Method 3 -- Neat Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Methyl Phthalate Diesters

The ester (100 mg, 3.42×10^{-5} mole) was placed in the bottom of a glass tube sealed at one end (15 cm x 0.4 mm OD) and centrifuged. The tube was bent in the shape of a Z,[28] and the sample end was immersed to the first elbow in an oil bath maintained at the desired temperature. The lower end (the second elbow) was simultaneously immersed in an ice bath, and as pyrolysis occurred, the olefins produced condensed

in the cold elbow. The olefins produced were sampled by syringe and analyzed by glc (column c, 70°) and the relative amount of each was determined by integration of the glc trace. The results are listed in Table VI.

Method 4 -- Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Methyl Phthalate Diesters in the Gas Chromatographic Instrument

The esters were injected as 20% solutions in ether under standard conditions using column c at 70°. The pyrolysis was considered to take place immediately in the injection port and the reported pyrolysis temperature is that of the injection port. The relative amount of each olefin was determined by integration of the glc trace and the results are listed in Table VI.

Partial Pyrolysis of ^{18}O Labelled cis- and trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate Esters in N,N-Dimethylformamide

The apparatus, reaction conditions, sample size (0.5-0.7 g), solvent volume (35 ml), and method used in the kinetic runs were employed here with the exception that there was no periodic sampling done. After the amount of time calculated (Appendix II) to result in the desired degree of ester decomposition, the flask was removed from the oil bath and its contents were immediately poured into a 500 ml, one-necked, round-bottomed flask which was immersed in an ice bath. The

solvent and any olefins produced were removed by trap to trap distillation (0.01 mm, pot 40°, trap-196°, mean free path 34 cm) leaving a viscous oily residue.

Neat Partial Pyrolysis of ^{18}O Labelled cis- and trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate Esters

A weighed amount (0.5-0.7 g) of the ester in fine crystalline form was placed in the bottom of a large test tube (2 cm x 15 cm) and immersed to a depth of 5 cm in an oil bath maintained at the desired temperature. After the amount of time calculated (Appendix II) to result in the desired degree of ester decomposition, the test tube was removed from the oil bath and cooled in an ice water bath. This resulted in a pale yellow solid residue containing both products and starting ester.

Purification of Partially Pyrolyzed ^{18}O Labelled cis- and trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate Esters

In order to obtain meaningful results in the analysis of the ^{18}O content of the product of the ester reduction w,w'-dihydroxy-o-xylene (DHX), the unpyrolyzed ester had to be completely separated from all other materials, particularly the phthalic acid generated in the pyrolysis. For this reason, the 70% pyrolysis residues produced above were subjected to the following treatment while the 20% and 0% pyrolysis residues were reduced without further

treatment.

The residue was first washed with 4 ml cold (0°) ether and any insoluble phthalic acid was removed by filtration. The ether solution was concentrated and the above procedure was repeated. The ether solution which resulted was concentrated to a volume of 1 ml and the ester was separated from all other materials by preparative tlc (ether on silica gel). This procedure yielded, upon removal of silica gel, a small amount (0.1-0.2 g) of pure, crystalline hydrogen phthalate ester.

Lithium Aluminum Hydride Reduction of ^{18}O Labelled cis- and trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate Esters

The hydrogen phthalate ester produced above (purified or unpurified) was dissolved in 50 ml anhydrous ether and placed in a 100 ml, three-necked, round-bottomed flask which was equipped with an efficient condenser (nitrogen inlet attached) and a magnetic stirrer. Lithium aluminum hydride (LAH) was added portionwise until all visible reaction had ceased and the solution was grey in colour (usually about 0.4 g LAH). The solution was stirred at 25° for 1 hr, and then at reflux temperature for 1 hr. The solution was then cooled to 0° and ethyl acetate was added dropwise until all reaction had ceased and the suspension which resulted was white in colour. The reaction was then worked up according to the procedure recommended by Fieser and Fieser[29] and the

crystalline precipitate which resulted was removed by filtration. The filtrate was washed twice with 20 ml portions of water, dried, and concentrated. This produced a viscous oil which, when treated with 10 ml of cold (0°) pentane, produced a two phase system. Repeated submersions in liquid nitrogen converted the lower layer into a solid crystalline mass (DHX) which was removed by filtration. The pentane layer was dried and concentrated, yielding about 30-60 mg of the 1,2-dimethylcyclohexanol. The cyclohexanol was analyzed by glc (column c, 90°) for geometrical isomerization, and a small sample (10 mg) was sent in a sealed vial for mass spectral analysis. The results of these two sets of analyses are reported in Tables VII, XIV and VIII, XV.

Purification of w,w'-Dihydroxy-o-xylene

The solid residue of DHX produced above in the 0 and 70 per cent pyrolyses was triturated with cold pentane and purified by preparative tlc (ether on silica gel). The residue produced in this manner was checked for identity and purity by analytical tlc (ether on silica gel, benzene on silica gel) against authentic, pure DHX. This procedure usually yielded about 10-20 mg of pure DHX, all of which was sent for mass spectral analysis to determine the atom per cent ^{18}O content (Appendix IV).

Determination of Per Cent Geometrical Isomerization in the Partial Pyrolysis of *cis*- and *trans*-1,2-Dimethylcyclohexyl Hydrogen Phthalate Esters

The alcohols produced by the LAH reduction of the ^{18}O labelled partially pyrolyzed hydrogen phthalate esters were analyzed for both geometrical isomers by glc as 20% solutions in chloroform using three columns of varying length and polarity (column a, 70°, column c, 90°, column e, 70°) in an attempt to obtain the most accurate results possible. The variation in relative peak areas from column to column was small but not insignificant, nor was it consistent from sample to sample. This variation was attributed to unknown contaminants whose presence was indicated by the poor baseline. Column c appeared to give the best separation and the most reproducible results. These are listed in Table VII for the neat pyrolyses and in Table XIV for the pyrolyses in DMF. Due to the very small amount of the minor alcohol and the poor baseline, these results may be taken only as maximum values.

APPENDIX I

Computer Program for the Analysis of Kinetic Data From the Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate Esters in Solvent

The following computer program "ENTACT" was used for the calculation of rate constants, activation parameters, and the errors in these values, for the pyrolysis of the cis- and trans-1,2-dimethylcyclohexyl hydrogen phthalate esters in solvent. The error in a particular value, as calculated using this program, is the difference between the "best" value (the reported value) and a "worst" value in which all the errors inherent in such calculations have been weighted in such a direction as to have a cumulative effect and produce the maximum possible value. This program contains a plotting subroutine which generates plots of ln ester left versus time for each kinetic run, and Arrhenius plots for each compound. The program, as reproduced, contains data card punching instructions and is fully commented, explaining all manipulations and operations. The program is written in FORTRAN IV and is for use with the IBM 360-50 computer.

```
      DOUBLE PRECISION SX,SY,SXY,SXX,SYY,C,SLOPE,YINT,XINT,STDERY,STDERXMAIN  10
     1,STDDEY,STDDEX,Y,X,CC,DSQRT,DABS,DLOG,DEXP,ESCONC,BASEN,ALIQOT,VBAMAIN  20
     2SE,TIME,TEMP,ESLEFT,EK,RK,EEA,EA,EARR,ARR,ES,S,WTSAMP,VSOLV,VEXPTLMAIN  30
     3,VBLANK,TERM1,VTHEOR,VCORR                                          MAIN  40
      DIMENSION Y(50),X(50),VBASE(50),TIME(50),EK(10),RK(10),ES(10),S(10MAIN  50
     1),TEMP(10),ESLEFT(50),VEXPTL(50)                                    MAIN  60
      DIMENSION SY(50),SX(50)                                             MAIN  70
C     DOUBLE PRECISION PROGRAM TO CALULATE1) CONCENTRATION OF ESTER        MAIN  80
C     AT T=0,2) MOLES ESTER LEFT AT ANY TIME T,3) RATE CONSTANT RK         MAIN  90
C     4) ERROR IN RATE CONSTANT EK,5)ENERGY OF ACTIVATION EA,6)            MAIN 100
C     ERROR IN ENERGY OF ACTIVATION EEA,7) ARRHENIUS PRE-EXPONENTIAL       MAIN 110
C     FACTOR ARR,8) ERROR IN ARRHENIUS PRE-EXPONENTIAL FACTOR EARR,        MAIN 120
C     ENTROPY OF ACTIVATION S,AND 10) ERROR IN ENTROPY OF ACTIVATION ES    MAIN 130
C     TWO SETS OF DATA ARE REQUIRED FOR TOTAL ERROR ANALYSIS.              MAIN 140
C     SECOND SET OF DATA WILL BE USED FOR EXACTLY SIMILAR CALCULATIONS     MAIN 150
C     BUT WILL INCLUDE STANDARD EXPERIMENTAL ERROR VALUES                  MAIN 160
C     ERROR ANALYSIS IS DESIGNED TO PRODUCE A MINIMUM OF CANCELLING        MAIN 170
C     OF ERRORS,SO THAT IN THE END THE 'E'VALUES OF THE SECOND RUN         MAIN 180
C     WILL SHOW A MAXIMUM DIFFERENCE FROM THE 'GOOD' VALUES.               MAIN 190
C     THERE ARE FIVE PARTS TO THIS PROGRAM.                                MAIN 200
C     1) MAIN PROGRAM FOR THE ABOVE MENTIONED CALCULATION                  MAIN 210
C     2) LEAST MEAN SQUARES (LMS) PROGRAM AS AN ACCESSORY PROGRAM TO       MAIN 220
C     THE MAIN PROGRAM.                                                    MAIN 230
C     3) PLOTTING PROGRAM 'MPLOT' (CURV)                                   MAIN 240
C     4) CONVERSION TO SINGLE PRECISION PROGRAM - AN ACCESSORY FOR         MAIN 250
C     MPLOT (SPRECN)                                                       MAIN 260
C     5) 'POT' AN ACCESSORY PROGRAM FOR MPLOT.                             MAIN 270
    1 READ 2,CMPD,ISOLIQ,NOTEMP                                           MAIN 280
    2 FORMAT(A4,I1,I3)                                                    MAIN 290
C     PUNCHING INPUT DATA.                                                 MAIN 300
C     CARD 1COMPOUND- COLUMNS 1-4 EG  TDME                                 MAIN 310
C     CARD 1 CONDITIONS COLUMNS  5  EG  1                                  MAIN 320
C     CARD 1 NUMBER OF TEMPERATURES  COL.  6-8 EG  4                       MAIN 330
C     CARD 2 SAMPLE WT.  COL. 2-7  EG  0.4806                              MAIN 340
C     CARD 2 SOLV. VOL. COL. 9-14  EG  39.24                               MAIN 350
C     CARD 2 BLANK VOL  COL.15-19  EG  00.19                               MAIN 360
C     CARD 2 BASE N.  COL. 21-27  EG  0.01218                              MAIN 370
C     CARD 2 NUMBER OF TIMES  COL.  29-30  EG  20                          MAIN 380
C     CARD 2 ALIQUOT SIZE  COL. 32-33  EG  1.                              MAIN 390
C     CARD 3-N  EXPERIMENTAL VOL. AND TIME IN THAT ORDER ,IN SERIES        MAIN 400
C     OF 6 DATA SETS PER CARD. EG  03840 00000 03940 00500 04040 01000     MAIN 410
C     USE COLUMNS 2-72                                                     MAIN 420
C     CARD 4 TEMPERATURES.  COL.  2-70  EG  3982 4032 4082 4132            MAIN 430
C     CARDS 2,3-N,ARE REPEATED FOR EACH SET OF DATA AND A DUPLICATE        MAIN 440
C     SET OF THESE IS REQUIRED FOR ERROR ANALYSIS.THE DUPLICATE SET        MAIN 450
C     FOLLOWS TEMPERATURE CARD 4                                           MAIN 460
C     CARD 5 THIS IS THE LAST CARD.--STOP1999  COL. 1-9                    MAIN 470
      IF (NOTEMP.EQ.999) STOP                                             MAIN 480
C     AFTER EACH DATA SET,GRAPH LABELLING CARDS ARE REQUIRED.              MAIN 490
C     CARD 1'LN(ESTER LEFT) VS . TIME -- DATA SET 1 'COL. 1-37             MAIN 500
C     CARD 2'LN ESTER LEFT' COL. 1-13                                      MAIN 510
C     CARD 2'TIME (SEC)'  COL. 59-67                                       MAIN 520
C     CARD 2' * '  COL.  19                                               MAIN 530
C     CARD 2'.+- '  COL.  76-78                                           MAIN 540
C     AFTER TEMPERATURE CARD 4 ,FOUR LABELLING CARDS FOR THE TWO           MAIN 550
C     ARRHENIUS PLOTS ARE REQUIRED.                                        MAIN 560
C     CARD 1 'LN EK) VS. 1./(R*TEMP)  COL. 1-22                            MAIN 570
C     CARD 2'LN(EK)'  COL. 1-6                                             MAIN 580
C     CARD 2'+'  COL.  19                                                  MAIN 590
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C      CARD 2'1./(R*TEMP)'    COL.  59-69                                  MAIN 600
C      CARD 2'.+-'  COL.  76-78                                            MAIN 610
C      CARD 3 'LN(RK) VS. 1./(R*TEMP)  COL. 1-22                           MAIN 620
C      CARD 4'LN(RK)'  COL. 1-6                                            MAIN 630
C      CARD 4'+'   COL.  19                                                MAIN 640
C      CARD 4'1./(R*TEMP)'    COL.  59-69                                  MAIN 650
C      CARD 4'.+-'  COL.  76-78                                            MAIN 660
C      THE ABOVE GRAPH CONTROL CARDS ARE REPEATED FOR THE ERROR ANALYSIS   MAIN 670
C      DATA SET (DUPLICATE) AND ARE THE SAME EXCEPT FOR THE ADDITION       MAIN 680
C      OF THE LABEL      '(ERROR ANALYSIS)'  WHICH FOLLOWS DIRECTLY        MAIN 690
C      THE HEADINGS ON THE DATA SET CARDS    COL.1-54                      MAIN 700
C      A SIMILAR HEADING FOLLOWS ON THE LABELLING CARDS (4) WHICH          MAIN 710
C      FOLLOW THE DATA SET CARDS OR THE ARRHENIUS PLOT.  COL. 1-39         MAIN 720
       K=0                                                                 MAIN 730
       IERROR=0                                                            MAIN 740
C      METHOD BY WHICH PROGRAM IS RECYCLED FOR EXPERIMENTAL ERROR          MAIN 750
C      ANALYSIS.IERROR VALUE DIRECTS COMPUTER DOWN DIFFERENT PATHS.        MAIN 760
       PRINT 105,CMPD                                                      MAIN 770
   105 FORMAT(1H1,A4)                                                      MAIN 780
     3 READ 4,WTSAMP,VSOLV,VBLANK,BASEN,NOTIME,ALIQOT                      MAIN 790
     4 FORMAT (F7.4,F6.2,F6.2,F8.5,I3,F3.0)                                MAIN 800
       PRINT 200,WTSAMP,VSOLV,VBLANK,BASEN,NOTIME,ALIQOT                   MAIN 810
   200 FORMAT(1H ,'SAMPLE WT.=', F7.4/1HO,'SOLVENT VOL.=',F6.2/1HO,'BLANKMAIN 820
      2 VOL.=',F6.2/1HO,'N BASE=',F8.5/1HO,'NO. OF TIMES=',I3/1HO,         MAIN 830
      3'ALIQOT=',F3.0)                                                     MAIN 840
       READ 300,(VEXPTL(I),TIME(I),I=1,NOTIME)                            MAIN 850
   300 FORMAT(6(F6.3,F6.2))                                                MAIN 860
C      PRINT OUT  TABLE HEADINGS FOR RAW INPUT DATA                        MAIN 870
       PRINT 310                                                           MAIN 880
   310 FORMAT(1H ,60X,'RAW INPUT DATA'/1HO,10X,'ML. BASE',10X,'TIME(MIN)'MAIN 890
      2/)                                                                  MAIN 900
C      PRINT OUT RAW INPUT DATA                                            MAIN 910
       PRINT 320,(VEXPTL(I),TIME(I),I=1,NOTIME)                            MAIN 920
   320 FORMAT(1H ,6X,1PD15.8,4X,1PD15.8)                                   MAIN 930
       PRINT 106                                                           MAIN 940
   106 FORMAT (1HO,10X,'CORRECTED INPUT DATA'/1HO,10X,'ML. BASE',11X,      MAIN 950
      1'TIME(MIN)', 9X,'MOLES ESTER LEFT'/)                                MAIN 960
       IF(IERROR.EQ.0)GO TO 340                                            MAIN 970
C      MODIFY RAW INPUT DATA('+' OR '-' ERROR)                             MAIN 980
C      THESE ARE EXPERIMENTAL ERROR VALUES WHOSE MAGNITUDE HAS BEEN        MAIN 990
C      DETERMINED BY MEASUREMENT OR ESTIMATION.                            MAIN1000
   330 WTSAMP=WTSAMP-0.0004D0                                              MAIN1010
       VSOLV=VSOLV+0.2D0                                                   MAIN1020
       VBLANK=VBLANK-0.02D0                                                MAIN1030
       BASEN=BASEN+0.0002D0                                                MAIN1040
       ALIQOT=ALIQOT+0.04D0                                                MAIN1050
C      PRINT OUT TABLE HEADINGS FOR 'CORRECTED'INPUT DATA                  MAIN1060
   340 TERM1=(WTSAMP*1000.D0)/(276.34D0*VSOLV)                             MAIN1070
C      TERM I IS  THEORETICAL CONCENTRATION OF ESTER IN REACTION           MAIN1080
C      CONSIDERING ONLY MEASURED WEIGHT AND CALCULATED VOLUME.             MAIN1090
       ESCONC=TERM1-((((VEXPTL(1)-VBLANK)*BASEN)-TERM1)/2.D0)              MAIN1100
C      ESCONC IS CALCULATED ESTER CONCENTRATION OF ESTER AT T=0,           MAIN1110
C      CONSIDERING THAT DURING DISSOLUTION,SOME ESTER MUST HAVE            MAIN1120
C      PYROLYZED.                                                          MAIN1130
C      CALCULATE'MOLES ESTER LEFT'FROM RAW INPUT DATA                      MAIN1140
       DO 9 I=1,NOTIME                                                     MAIN1150
       IF(IERROR.EQ.1)VEXPTL(I)=VEXPTL(I)+0.10D0                           MAIN1160
       VBASE(I)=ESCONC/BASEN                                               MAIN1170
       VCORR=VEXPTL(I)-VBASE(I)                                            MAIN1180
C      VCORR IS AMOUNT OF BASE NECESSARY TO TITRATE SOLVENT BLANK          MAIN1190
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C      PLUS ANY PHTHALIC ACID  PRODUCED DURING DISSOLUTION PYROLYSIS.     MAIN1200
C      MODIFY DATA FOR ERROR CALCULATION - MAXIMIZE 'ESLEFT(I)'          MAIN1210
       IF (IERROR.EQ.1) GO TO 400                                        MAIN1220
       VBASE(I)=VEXPTL(I)-VCORR                                          MAIN1230
       GO TO 410                                                         MAIN1240
  400  VBASE(I)=(VEXPTL(I)-2.D0*0.10D0) - VCORR                          MAIN1250
C      MODIFY TIME(I)FOR ERROR CALCULATION                               MAIN1260
  410  IF(IERROR.EQ.1)TIME(I)=TIME(I)+0.05                               MAIN1270
C      CODE FOR PYROLYSIS CONDITIONS-NUMBER COMES DIRECTLY AFTER NAME FORMAIN1280
C      COMPOUND -DESCRIBES PYROLYSIS CONDITIONS- NEAT,SOLVENT,MONO       MAIN1290
C      OR DIESTER                                                        MAIN1300
C      SET ISOLIQ=0,FOR A SOLID                                          MAIN1310
C      SET ISOLIQ=1,FOR A LIQUID                                         MAIN1320
C      SET ISOLIQ=2,FOR ALIQUID(DIESTER)                                 MAIN1330
       IF(ISOLIQ-1)20,21,23                                              MAIN1340
C      EQUATIONS USED TO CALCULATE MOLES ESTER LEFT DEPENDING ON ABOVE   MAIN1350
C      STATED CONDITIONS.                                                MAIN1360
   20  ESLEFT(I)=2.D0*ESCONC-(BASEN*VBASE(I)/1000.D0)                    MAIN1370
       GO TO 22                                                          MAIN1380
   21  ESLEFT(I)=2.D0*ESCONC*ALIQOT/1000.D0-(BASEN*VBASE(I)/1000.D0)     MAIN1390
       GO TO 22                                                          MAIN1400
   23  ESLEFT(I)=ESCONC*ALIQOT/1000.D0-(BASEN*VBASE(I)/1000.D0)          MAIN1410
C      PRINT OUT 'CORRECTED'INPUT DATA AND'MOLES ESTER LEFT'             MAIN1420
   22  PRINT 107,VBASE(I),TIME(I),ESLEFT(I)                             MAIN1430
  107  FORMAT(1H 6X,D15.8,4X,D15.8,6X,D15.8)                             MAIN1440
       Y(I)=DLOG(ESLEFT(I))                                              MAIN1450
       X(I)=TIME(I)*60.                                                  MAIN1460
    9  CONTINUE                                                          MAIN1470
       CALL SPRECN(Y,X,NOTIME,SY,SX)                                     MAIN1480
C      CONVERT DOUBLE PRECISION NUMBERS TO SINGLE PRECISION FOR          MAIN1490
       CALL MINMAX (SX,SY,NOTIME,XMIN,XMAX,YMIN,YMAX)                    MAIN1500
       CALL MPLOT (SX,XMIN,XMAX,0,SY,YMIN,YMAX,0,Z,0.,0.,0,NOTIME,1,1,2) MAIN1510
C      PLOT ROUTINE.                                                     MAIN1520
C      PLOT ROUTINE FOR PLOTTING ALL GRAPHS.                             MAIN1530
       CALL LMS(Y,X,  NOTIME,SLOPE,YINT,XINT,CC,STDERY,STDERX)           MAIN1540
       K=K+1                                                             MAIN1550
C      ALTER Y- AND X- INTERCEPTS TO MAXIMIZE SLOPES,AND HENCE K'S AND   MAIN1560
C      EVENTUALLY MAXIMIZE 'A'                                           MAIN1570
C      USE TWO STANDARD DEVIATIONS IN ORDER TO BE SURE TO INCORPORATE    MAIN1580
C      MOST DATA-95%.                                                    MAIN1590
       EK(K)=(YINT+2.D0*STDERY)/(XINT-2.D0*STDERX)                       MAIN1600
C      STANDARD DEVIATIONS AND EXPERIMENTAL ERRORS ARE WEIGHTED IN       MAIN1610
C      SUCH A DIRECTION AS TO PRODUCE A CUMULATIVE EFFECT,RESULTING      MAIN1620
C      IN A MAXIMUM ERROR VALUE.                                         MAIN1630
       RK(K)=-SLOPE                                                      MAIN1640
       PRINT 100,K,CC,K,STDERY,K,STDERX,K,EK(K),K,RK(K)                  MAIN1650
  100  FORMAT(1HO,3HCC(,I2,2H)=,D15.8/1HO,7HSTDERY(,I2,2H)=,D15.8,10X,7HSMAIN1660
     1TDERX(,I2,2H)=,D15.8/1HO,3HEK(,I2,2H)=,D15.8,1X,5HSEC-1/1HO,3HRK(,MAIN1670
     2I2,2H)=,D15.8,1X,5HSEC-1//)                                      MAIN1680
       IF(K.LT.NOTEMP)GO TO 3                                            MAIN1690
    7  IF(IERROR.EQ.0)READ 8,(TEMP(K),K=1,NOTEMP)                        MAIN1700
    8  FORMAT (14F5.1)                                                   MAIN1710
       DO 10 K=1,NOTEMP                                                  MAIN1720
       PRINT 110,K,TEMP(K)                                               MAIN1730
  110  FORMAT(1HO,5HTEMP(,I2,2H)=,F6.1,1X,5HDEG K)                       MAIN1740
C      MODIFY'TEMP(K)'FOR ERROR CALCULATION                              MAIN1750
       IF (IERROR.EQ.1) TEMP(K)=TEMP(K)+0.2D0                            MAIN1760
       Y(K)=DLOG(EK(K))                                                  MAIN1770
        X(K)=1./(1.98717D0*TEMP(K))                                      MAIN1780
   10  CONTINUE                                                          MAIN1790
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```
      CALL SPRECN(Y,X,NOTEMP,SY,SX)                                          MAIN1800
      CALL MINMAX (SX,SY,NOTEMP,XMIN,XMAX,YMIN,YMAX)                         MAIN1810
      CALL MPLOT (SX,XMIN,XMAX,0,SY,YMIN,YMAX,0,Z,0.,0.,0,NOTEMP,1,1,2)      MAIN1820
      CALL LMS(Y,X,  NOTEMP,SLOPE,YINT,XINT,CC,STDERY,STDERX)                MAIN1830
      PRINT 500,STDERY,STDERX                                                MAIN1840
  500 FORMAT(1HO,'STANDARD ERROR IN Y=',D15.8,10X,'STANDARD ERROR IN X       MAIN1850
     1=',D15.8)                                                              MAIN1860
C     ALTER Y- AND X- INTERCEPTS TO MAXIMIZE EA,AND EARR                     MAIN1870
      EEA=(YINT+2.D0*STDERY)/(XINT-2.D0*STDERX)                              MAIN1880
      EARR=DEXP(YINT+2.D0*STDERY)                                            MAIN1890
      DO 30 K=1,NOTEMP                                                       MAIN1900
      IF((K.EQ.1).AND.(IERROR.EQ.1))YINT=YINT+2.D0*STDERY                    MAIN1910
      ES(K)=1.98717D0*DLOG(6.6256D-27/(1.38054D-16*2.718282D0*TEMP(K)))+MAIN1920
     1(1.98717*YINT)                                                         MAIN1930
      PRINT 101,K,ES(K)                                                      MAIN1940
  101 FORMAT(1H ,3HES(,I2,2H)=,D15.8,1X,13HCALS/MOLE/DEG)                    MAIN1950
   30 CONTINUE                                                               MAIN1960
      PRINT 102,EEA,EARR,CC                                                  MAIN1970
  102 FORMAT(1HO,4HEEA=,D15.8,1X,9HCALS/MOLE/1HO,5HEARR=,D15.8/1HO,4HECCMAIN1980
     1=,D15.8//)                                                             MAIN1990
      DO 11 K=1,NOTEMP                                                       MAIN2000
      Y(K)=DLOG(RK(K))                                                       MAIN2010
       X(K)=1./(1.98717D0*TEMP(K))                                           MAIN2020
   11 CONTINUE                                                               MAIN2030
      CALL SPRECN(Y,X,NOTEMP,SY,SX)                                          MAIN2040
      CALL MINMAX (SX,SY,NOTEMP,XMIN,XMAX,YMIN,YMAX)                         MAIN2050
      CALL MPLOT (SX,XMIN,XMAX,0,SY,YMIN,YMAX,0,Z,0.,0.,0,NOTEMP,1,1,2)      MAIN2060
      CALL LMS(Y,X,  NOTEMP,SLOPE,YINT,XINT,CC,STDERY,STDERX)                MAIN2070
      PRINT 500,STDERY,STDERX                                                MAIN2080
      EA=-SLOPE                                                              MAIN2090
      ARR=DEXP(YINT)                                                         MAIN2100
      DO 12 K=1,NOTEMP                                                       MAIN2110
      IF((K.EQ.1).AND.(IERROR.EQ.1))YINT=YINT+2.D0*STDERY                    MAIN2120
       S(K)=1.98717D0*DLOG(6.6256D-27/(1.38054D-16*2.718282D0*TEMP(K)))+MAIN2130
     1(1.98717*YINT)                                                         MAIN2140
      PRINT 103,K,S(K)                                                       MAIN2150
  103 FORMAT(1H ,2HS(,I2,2H)=,D15.8,1X,13HCALS/DEG/MOLE)                     MAIN2160
   12 CONTINUE                                                               MAIN2170
      PRINT 104,EA,ARR,CC                                                    MAIN2180
  104 FORMAT(1HO,3HEA=,D15.8,1X,9HCALS/MOLE/1HO,4HARR=,D15.8/1HO,3HCC=,DMAIN2190
     115.8)                                                                  MAIN2200
C     SET SUBSCRIPT COUNTER 'K' BACK TO ZERO                                 MAIN2210
      K=0                                                                    MAIN2220
      IERROR=IERROR+1                                                        MAIN2230
      IF(IERROR.EQ.2)GO TO 1                                                 MAIN2240
      GO TO 3                                                                MAIN2250
      END                                                                    MAIN2260
      SUBROUTINE LMS(Y,X,  N,SLOPE,YINT,XINT,CC,STDERY,STDERX)               LMS   10
C     LEAST MEAN SQUARES SUBROUTINE ****EBCDIC**** DOUBLE PRECISION          LMS   20
      DOUBLE PRECISION SX,SY,SXY,SXX,SYY,C,SLOPE,YINT,XINT,STDERY,STDERXLMS   30
     1,STDDEY,STDDEX,Y,X,CC,DSQRT,DABS                                       LMS   40
      DIMENSION Y(50),X(50)                                                  LMS   50
      SX=0.                                                                  LMS   60
      SY=0.                                                                  LMS   70
      SXY=0.                                                                 LMS   80
      SXX=0.                                                                 LMS   90
      SYY=0.                                                                 LMS  100
      DO 900 I=1,N                                                           LMS  110
      SX=SX+X(I)                                                             LMS  120
      SY=SY+Y(I)                                                             LMS  130
```

```
      SXY=SXY+X(I)*Y(I)                                                 LMS  140
      SXX=SXX+X(I)*X(I)                                                 LMS  150
      SYY=SYY+Y(I)*Y(I)                                                 LMS  160
  900 CONTINUE                                                          LMS  170
      C=N                                                               LMS  180
      SLOPE=(SX*SY-C*SXY)/(SX*SX-C*SXX)                                 LMS  190
      YINT=(SX*SXY-SXX*SY)/(SX*SX-C*SXX)                                LMS  200
      XINT=-YINT/SLOPE                                                  LMS  210
      STDDEY=DSQRT(SYY/C-(SY/C)*(SY/C))                                 LMS  220
      STDDEX=DSQRT(SXX/C-(SX/C)*(SX/C))                                 LMS  230
      CC=((SXY/C)-(SX/C)*(SY/C))/(STDDEY*STDDEX)                        LMS  240
      IF(DABS(CC)-1.D0) 901,902,902                                     LMS  250
  901 STDERY=STDDEY*DSQRT(1.D0-CC*CC)                                   LMS  260
      STDERX=STDDEX*DSQRT(1.D0-CC*CC)                                   LMS  270
      GO TO 904                                                         LMS  280
  902 STDERY=0.                                                         LMS  290
      STDERX=0.                                                         LMS  300
      PRINT 903                                                         LMS  310
  903 FORMAT(1H ,15HABS(CC) IS.GE.1)                                    LMS  320
  904 WRITE (     6,905) SLOPE,YINT,XINT,CC,STDERY,STDERX               LMS  330
  905 FORMAT (1H0,41X,'SLOPE=',1PD15.8/1H ,35X,'Y-INTERCEPT=',1PD15.8   LMS  340
     1/1H ,35X,'X-INTERCEPT=',1PD15.8/1H ,23X,'CORRELATION COEFFICIENT='LMS  350
     2,1PD15.8/1H ,'STANDARD ERROR OF ESTIMATE FOR Y-AXIS VARIABLE=',   LMS  360
     31PD15.8/1H ,'STANDARD ERROR OF ESTIMATE FOR X-AXIS VARIABLE=',    LMS  370
     41PD15.8)                                                          LMS  380
C     $$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$ PRINT       LMS  390
      RETURN                                                            LMS  400
      END                                                               LMS  410
      SUBROUTINE SPRECN(Y,X,N,SY,SX)                                    SPRN  10
      DOUBLE PRECISION Y(1),X(1)                                        SPRN  20
      DIMENSION SY(1),SX(1)                                             SPRN  30
      DO 100 I=1,N                                                      SPRN  40
      SY(I)=SNGL(Y(I))                                                  SPRN  50
      SX(I)=SNGL(X(I))                                                  SPRN  60
  100 CONTINUE                                                          SPRN  70
      RETURN                                                            SPRN  80
      END                                                               SPRN  90
      SUBROUTINE MPLOT(X,XMIN,XMAX,LX,Y,YMIN,YMAX,LY,Z,ZMIN,ZMAX,LZ,NPT,PLOT  10
     1NPLOT,NCOPY,NDIM)                                                 PLOT  20
      DIMENSION SX(13),TITLE(80),IYAXIS(18),NCH(41),XAXIS(17),L(140),X(1PLOT  30
     1),Y(1),Z(1),PX(120),PY(120),PZ(120)                               PLOT  40
C     THIS IS A GENERAL PLOTTING SUBROUTINE WHERE X,Y, AND Z ARE SINGLE PLOT  50
C     SUBSCRIPTED VARIABLES IDENTIFYING THE COORDINATES OF THE POINTS TOPLOT  60
C     BE PLOTTED. XMIN,YMIN, AND ZMIN ARE THE MINIMUM VALUES, AND XMAX, PLOT  70
C     YMAX, AND ZMAX CORRESPOND TO THE MAXIMUM VALUES ON THE X,Y, AND Z PLOT  80
C     AXES. LX,LY, AND LZ DEFINE THE TYPE OF SCALE USED ALONG THE X,Y,  PLOT  90
C     AND Z AXES AS FOLLOWS---0(LINEAR), 1(ONE CYCLE LOG), 2(TWO CYCLE  PLOT 100
C     LOG), ETC., MAXIMUM NO. OF (6)  NOTE: WHEN LX,LY, AND LZ ARE OTHERPLOT 110
C     THAN 0  THE XMIN, YMIN, AND ZMIN SHOULD BE OTHER THAN 0.0 .       PLOT 120
C               NPT IS THE TOTAL NUMBER OF POINTS TO BE PLOTTED. NPLOT  PLOT 130
C     IS THE NUMBER OF TWO DIMENSIONAL RELATIONSHIPS (CURVES) WHICH ARE PLOT 140
C     TO BE PLOTTED, THE MAXIMUM VALUE IS 40. NCOPY IS THE NUMBER OF    PLOT 150
C     PLOTS TO BE PRINTED. NDIM IS THE DIMENSIONALITY OF THE FUNCTION   PLOT 160
C     TO BE PLOTTED. IF NDIM=3 TOPOGRAPHIC MAPPING OF A 3-DIMENSIONAL   PLOT 170
C     SURFACE ONTO THE X-Y PLANE OCCURS.                                PLOT 180
C                                                                       PLOT 190
C     EXPLANATION OF INPUT DATA:                                        PLOT 200
C                                                                       PLOT 210
C          CARD 1 - COL.   1-80 TITLE OF GRAPH                          PLOT 220
C          CARD 2 - COL.   1-18 TITLE OF YAXIS                          PLOT 230
```

```
C                          19-58 CHARACTERS USED IN PLOT (THE CHARACTERS PLOT 240
C                                USED IN THE GRAPH ARE DETERMINED BY THE PLOT 250
C                                ORDER OF THE CHARACTERS IN COL. 19-58,  PLOT 260
C                                THE NUMBER OF TWO DIMENSIONAL RELATION- PLOT 270
C                                SHIPS REQUESTED, AND THE DIMENSIONALITY PLOT 280
C                                OF THE FUNCTION TO BE PLOTTED.)         PLOT 290
C                          59-75 TITLE OF XAXIS                          PLOT 300
C                          76    '.'                                     PLOT 310
C                          77    '+'                                     PLOT 320
C                          78    '-'                                     PLOT 330
C                          79    BLANK                                   PLOT 340
    1 FORMAT (80A1)                                                      PLOT 350
    2 FORMAT (18A1,40A1,17A1,4A1)                                        PLOT 360
    3 FORMAT (1H1,80A1)                                                  PLOT 370
    4 FORMAT (1H ,A1,1PE9.2,121A1)                                       PLOT 380
    5 FORMAT (132A1)                                                     PLOT 390
    6 FORMAT (5X,2(1PE9.2),10(1X,1PE9.2),1PE9.2)                         PLOT 400
    7 FORMAT(1PE15.1,E117.1)                                             PLOT 410
   8  FORMAT(1PE15.1,E61.1,E56.1)                                        PLOT 420
    9 FORMAT(1PE15.1,2E40.1,E37.1)                                       PLOT 430
   10 FORMAT(1PE15.1,3E30.1,E27.1)                                       PLOT 440
   11 FORMAT(1PE15.1,4E24.1,E21.1)                                       PLOT 450
   12 FORMAT(1H0,57X,17A1)                                               PLOT 460
      LLX=LX+1                                                           PLOT 470
      JREAD5=5                                                           PLOT 480
      JRITE6=6                                                           PLOT 490
   13 READ      (JREAD5, 1) (TITLE(I),I=1,80)                          PLOT 500
   14 READ (JREAD5,2) (IYAXIS(I),I=1,18),(NCH(I),I=1,40),(XAXIS(I),I=1,1PLOT 510
     17),ND,NP,NM,NB                                                     PLOT 520
      DO 9999 I=1,NPT                                                    PLOT 530
      PX(I)=X(I)                                                         PLOT 540
      PY(I)=Y(I)                                                         PLOT 550
      IF (NDIM.EQ.3) PZ(I)=Z(I)                                          PLOT 560
 9999 CONTINUE                                                           PLOT 570
   15 NCH(41)=NB                                                         PLOT 580
      NPN=NPT/NPLOT                                                      PLOT 590
      IF(LX.GT.0)GOTO17                                                  PLOT 600
 1717 CX=120./(XMAX-XMIN)                                                PLOT 610
      SX(1)=XMIN                                                         PLOT 620
      SX(13)=XMAX                                                        PLOT 630
      U=XMIN                                                             PLOT 640
      DO16K=2,12                                                         PLOT 650
      U=(XMAX-XMIN)/12.+U                                                PLOT 660
   16 SX(K)=U                                                            PLOT 670
      XMIM = XMIN                                                        PLOT 680
      GOTO19                                                             PLOT 690
   17 XLX=LX                                                             PLOT 700
      CX=120./XLX                                                        PLOT 710
      NX= ALOG10(XMIN)                                                   PLOT 720
      IF(XMIN.LT.1.0)NX= ALOG10(XMIN)-0.99999999                         PLOT 730
 1818 DO18K=1,LLX                                                        PLOT 740
   18 SX(K)= 10.**(NX+K-1)                                               PLOT 750
      XMIM= SX(1)                                                        PLOT 760
   19 CALL POT (PX,XMIM,LX,NPT,0,120.,CX)                                PLOT 770
      IF(LY.GT.0)GOTO20                                                  PLOT 780
 2020 CY=50./(YMAX-YMIN)                                                 PLOT 790
      GOTO21                                                             PLOT 800
   20 YLY=LY                                                             PLOT 810
      CY=50./YLY                                                         PLOT 820
      KY=CY                                                              PLOT 830
```

```
      NY= ALOG10(YMIN)                                                  PLOT  840
      IF(YMIN.LT.1.0)NY= ALOG10(YMIN)-0.99999999                        PLOT  850
 2121 YMIN= 10.**NY                                                     PLOT  860
   21 CALL POT (PY,YMIN,LY,NPT,1,50.,CY)                              PLOT  870
      IF(NDIM.LT.3)GOTO24                                               PLOT  880
 2424 IF(LZ.GT.0)GOTO22                                                 PLOT  890
      CZ=40./(ZMAX-ZMIN)                                                PLOT  900
      GOTO23                                                            PLOT  910
   22 ZLZ=LZ                                                            PLOT  920
      CZ=40./ZLZ                                                        PLOT  930
   23 CALL POT (PZ,ZMIN,LZ,NPT,0,40.,CZ)                              PLOT  940
   24 DO50NN=1,NCOPY                                                    PLOT  950
      M1=1                                                              PLOT  960
      T1=33.                                                            PLOT  970
      LYY=LY                                                            PLOT  980
      TT=50.                                                            PLOT  990
      WRITE        (JRITE6, 3) (TITLE(I),I=1,80)                        PLOT1000
      DO43KK=1,51                                                       PLOT1010
      N=1                                                               PLOT1020
      NNN=NPN                                                           PLOT1030
      JED=1                                                             PLOT1040
      T=51-KK                                                           PLOT1050
      DO25J=1,133                                                       PLOT1060
   25 L(J)=NB                                                           PLOT1070
      L(133)=ND                                                         PLOT1080
      IF(LY.GT.0)GOTO26                                                 PLOT1090
 2626 L(13)=ND                                                          PLOT1100
      IF(T.GT.TT)GOTO30                                                 PLOT1110
 3030 SCALE=T/CY+YMIN                                                   PLOT1120
      L(133)=NP                                                         PLOT1130
      N=0                                                               PLOT1140
      TT=TT-5.                                                          PLOT1150
      IF(T.LE.0.)SCALE=YMIN                                             PLOT1160
  303 GOTO30                                                            PLOT1170
   26 GOTO(27,27,28,28,27,28),LY                                        PLOT1180
   27 SS=KY*LYY                                                         PLOT1190
      GOTO29                                                            PLOT1200
   28 SS=KY*LYY+1                                                       PLOT1210
   29 L(13)=ND                                                          PLOT1220
      IF(T.GT.SS)GOTO30                                                 PLOT1230
 2929 SCALE=10.**(NY+LYY)                                               PLOT1240
      N=0                                                               PLOT1250
      LYY=LYY-1                                                         PLOT1260
      L(13)=NP                                                          PLOT1270
      L(133)=NP                                                         PLOT1280
   30 IF(50..EQ.T)GOTO31                                                PLOT1290
  313 IF(0..NE.T)GOTO37                                                 PLOT1300
   31 DO32J=14,133                                                      PLOT1310
   32 L(J)=NM                                                           PLOT1320
      IF(LX.GT.0)GOTO34                                                 PLOT1330
  444 DO33J=13,133,10                                                   PLOT1340
   33 L(J)=NP                                                           PLOT1350
      GOTO36                                                            PLOT1360
   34 KX=120/LX                                                         PLOT1370
      DO35J=13,133,KX                                                   PLOT1380
   35 L(J)=NP                                                           PLOT1390
   36 IF(50..EQ.T)L(133)=NP                                             PLOT1400
   37 DO40LM=1,NPLOT                                                    PLOT1410
      DO39I=JED,NNN                                                     PLOT1420
      IF (PY(I).NE.T) GO TO 39                                          PLOT1430
```

```
 9393 J=PX(I)                                                          PLOT1440
      IF(NDIM.NE.3)GOTO38                                              PLOT1450
 8383 IZ=PZ(I)                                                         PLOT1460
      L(J+13)=NCH(IZ+1)                                                PLOT1470
      GOTO39                                                           PLOT1480
   38 L(J+13)=NCH(LM)                                                  PLOT1490
   39 CONTINUE                                                         PLOT1500
      JED=NNN+1                                                        PLOT1510
      NNN=NNN+NPN                                                      PLOT1520
   40 CONTINUE                                                         PLOT1530
      IF (N.EQ.0) L(13)=NP                                             PLOT1540
      IF(T1.NE.T)GOTO41                                                PLOT1550
  411 IF(15..GE.T)GOTO41                                               PLOT1560
  412 L(2)=IYAXIS(M1)                                                  PLOT1570
      M1=M1+1                                                          PLOT1580
      T1=T1-1.                                                         PLOT1590
   41 IF(N.EQ.1)GOTO42                                                 PLOT1600
 2420 WRITE        (JRITE6, 4) L(2),SCALE,(L(J),J=13,133)             PLOT1610
      GOTO43                                                           PLOT1620
   42 WRITE        (JRITE6, 5) (L(J),J=1,2),(L(I),I=4,133)            PLOT1630
   43 CONTINUE                                                         PLOT1640
      GOTO(44,45,46,47,48,49,44),LLX                                   PLOT1650
   44 WRITE        (JRITE6, 6) (SX(K),K=1,13)                         PLOT1660
      GOTO50                                                           PLOT1670
   45 WRITE        (JRITE6, 7) (SX(K),K=1,LLX)                        PLOT1680
      GOTO50                                                           PLOT1690
   46 WRITE        (JRITE6, 8) (SX(K),K=1,LLX)                        PLOT1700
      GOTO50                                                           PLOT1710
   47 WRITE        (JRITE6, 9) (SX(K),K=1,LLX)                        PLOT1720
      GOTO50                                                           PLOT1730
   48 WRITE        (JRITE6,10) (SX(K),K=1,LLX)                        PLOT1740
      GOTO50                                                           PLOT1750
   49 WRITE        (JRITE6,11) (SX(K),K=1,LLX)                        PLOT1760
   50 WRITE      (JRITE6, 12) (XAXIS(I),I=1,17)                       PLOT1770
      RETURN                                                           PLOT1780
      END                                                              PLOT1790
      SUBROUTINEPOT(G,VMIN,LV,NP,J,VC,C)                               POT    10
      DIMENSIONG(1)                                                    POT    20
      IF(LV.GT.0)GOTO2                                                 POT    30
   22 DO1I=1,NP                                                        POT    40
    1 G(I)=FLOAT(IFIX(C*(G(I)-VMIN)+.5))                               POT    50
      GOTO4                                                            POT    60
    2 DO3I=1,NP                                                        POT    70
    3 G(I)=FLOAT(IFIX(C*(ALOG10(G(I)/VMIN)        )+.5))               POT    80
    4 IF(J.GT.0)GOTO7                                                  POT    90
   77 DO6I=1,NP                                                        POT   100
      IF(G(I).LT.0.)GOTO5                                              POT   110
   55 IF(G(I).LE.VC)GOTO6                                              POT   120
    5 G(I)=VC+1.                                                       POT   130
    6 CONTINUE                                                         POT   140
    7 RETURN                                                           POT   150
      END                                                              POT   160
      SUBROUTINE MINMAX(X,Y,N,XMIN,XMAX,YMIN,YMAX)                     MINM   10
C*************************************************************************MINM   20
C                                                                      MINM   30
C     SUBROUTINE TO CALCULATE MINIMUM AND MAXIMUM VALUES OF ARRAY      MINM   40
C     MEMBERS FOR USE WITH PLOTTING ROUTINE (I.E. SUBROUTINE MPLOT)    MINM   50
C                                                                      MINM   60
C     'CALL MINMAX(...)' SHOULD IMMEDIATELY PRECEDE 'CALL MPLOT(...)'  MINM   70
C                                                                      MINM   80
```

```
C     ..................................................................MINM  90
C                          TABLE OF VARIABLES                          MINM 100
C                                                                      MINM 110
C                                                                      MINM 120
C     X         X - ARRAY                                              MINM 130
C     Y         Y - ARRAY                                              MINM 140
C     N         NUMBER OF ARRAY MEMBERS                                MINM 150
C     XMIN      SMALLEST X - ARRAY MEMBER                              MINM 160
C     XMAX      LARGEST X - ARRAY MEMBER                               MINM 170
C     YMIN      SMALLEST Y - ARRAY MEMBER                              MINM 180
C     YMAX      LARGEST Y - ARRAY MEMBER                               MINM 190
C     ..................................................................MINM 200
C                                                                      MINM 210
C**********************************************************************MINM 220
      DIMENSION X(1),Y(1)                                              MINM 230
      XMIN=X(1)                                                        MINM 240
      XMAX=X(1)                                                        MINM 250
      YMIN=Y(1)                                                        MINM 260
      YMAX=Y(1)                                                        MINM 270
      DO 10 I=2,N                                                      MINM 280
      IF (X(I).LT.XMIN) XMIN=X(I)                                      MINM 290
      IF (X(I).GT.XMAX) XMAX=X(I)                                      MINM 300
      IF (Y(I).LT.YMIN) YMIN=Y(I)                                      MINM 310
      IF (Y(I).GT.YMAX) YMAX=Y(I)                                      MINM 320
   10 CONTINUE                                                         MINM 330
      XDIFF=ABS(XMAX-XMIN)                                             MINM 340
      YDIFF= ABS(YMAX-YMIN)                                            MINM 350
      XADD=0.05*XDIFF                                                  MINM 360
      YADD=0.05*YDIFF                                                  MINM 370
C     INCREMENT TO AVOID PLOTTING POINTS ON THE AXIS                   MINM 380
      XMAX=XMAX+XADD                                                   MINM 390
      XMIN=XMIN-XADD                                                   MINM 400
      YMAX=YMAX+YADD                                                   MINM 410
      YMIN=YMIN-YADD                                                   MINM 420
      RETURN                                                           MINM 430
      END                                                              MINM 440
```

The computer program reproduced above was written specifically for the kinetic study of the pyrolysis of cis- and trans-1,2-dimethylcyclohexyl hydrogen phthalate esters in solvent. In order to be used for other esters, or under other conditions, it must be altered in the following manner.

A Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Methyl Phthalate Diesters in N,N-Dimethylformamide

Substitute the following cards in the "MAIN" program:

```
Card  1070    TERM1=(WTSAMP*1000.DO)/(290.37DO*VSOLV)
      1100    ESCONC=TERM1-((VEXPTL(1)-VBLANK)*BASEN)
      1170    eliminate this card
      1180    VCORR=VEXPTL(1)
      1220    eliminate this card
      1250    eliminate this card
```

These last two cards are part of the error analysis sequence, and their purpose is to take account of the experimental error in large titrations. They are removed in this case because they would result in titrations of negative volumes in the case of methyl ester pyrolysis.

B Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Methyl Phthalate Diesters Neat

Substitute the following cards in the "MAIN" program:

```
Card  1070     TERM1=WTSAMP/290.37
      1100     ESCONC=TERM1-((VEXPTL(1)-VBLANK)*BASEN)
      1170     eliminate this card
      1180     VCORR=VEXPTL(1)
      1370     ESLEFT(I)=ESCONC-(BASEN*VBASE(I)/1000.DO)
```

APPENDIX II

Calculation of the Duration of Partial Pyrolysis

First-order kinetics were assumed to be followed throughout the full extent of the reaction; therefore, the first-order rate equation was used:

$$\ln E_L = - kt + \ln E_o$$

which may be rearranged to give:

$$t = \frac{- \ln (E_L/E_o)}{k}$$

where all terms are as previously defined.

In order to calculate the necessary length of time to achieve a certain per cent pyrolysis at a specified temperature, the appropriate values for the ratio E_L/E_o and the rate constant (k) are substituted into the above equation.

Example:

For the 70% pyrolysis of the cis-ester at 120° neat, the values are $E_L/E_o = 0.30$ and $k = 60.61\ sec^{-1}$.

$$t = \frac{- \ln (0.30)}{60.61} = 2010\ sec$$

APPENDIX III

Calculation of Per Cent ^{18}O Exchange

The amount of ^{18}O in each sample was determined by mass spectral analysis under the following conditions: GLC -- column 6' x ¼", glass, 3% SE 30, on Chromosorb W, HP, Temperature -- 90° + 4°/min, flow -- 20 ml He/min, injector -- 280°, separator -- 280°; Mass spectrum, ion source --290°, 70 ev, 60 μ amps.

Once the mass spectra have been obtained on the samples, there are four steps involved in obtaining the per cent exchange values:

1. The measurement of peak heights and the errors involved in measurement.
2. The calculation of the ratios M + 2/M and the maximum and minimum values of M + 2/M.
3. The calculation of the maximum, best and worst values of per cent ^{18}O content.
4. The calculation of the per cent exchange values.

1. Measurement of Peak Heights

This was done with a well calibrated rule which contained one millimeter divisions. The errors were measured at the same time and are actually an estimate of how accurately straight lines may be drawn through the tops and bottoms of

the various peaks and then, how accurately may the distance between them be measured. As such, these values are maximum estimates and are intended to represent the worst possible range of error. In a similar manner, the reported values may be regarded as "best" values. An example of a typical set of peak height measurements follows:

M	=	19.7 ± 0.2	mm	Sensitivity	10
M + 1	=	17.0 ± 0.5	"	"	100
M + 1	=	1.8 ± 0.1	"	"	10
M + 2	=	4.0 ± 0.3	"	"	100

2. Calculation of the Ratio M + 2/M, and Errors

As may be seen in the above example, most of the mass spectrum peak heights were measured on two different sensitivity scales. Therefore, in order to calculate an estimate of the error, they must be converted to the same sensitivity scale. This was done by use of a peak whose height could be accurately measured on both sensitivity scales as an indicator of the error to be expected in converting from one sensitivity scale to the other. The peak usually used for this purpose was the M + 1 peak. An example of how the maximum, reported and minimum values were calculated follows.

Reported Value: A "best value", calculated from the actual measurement of the peak height.

e.g. $(M + 2/M) \times 100 = \left[(4.0/10)/19.7\right] \times 100 = 2.030\%$

Maximum Value: A "worst value", in which all the errors have been weighted in such a direction as to have a cumulative effect and produce the maximum possible value.

$$\text{e.g.} \quad (M + 2/M) \times 100 = \left[\frac{(4.0 + 0.3)\ (1.8 + 0.1)}{(17.0 - 0.5)} \Big/ (19.7 - 0.2) \right]$$

$$\times 100 = 2.540\%$$

Minimum Value: A "worst value", in which all the errors have been weighted in such a direction as to have a cumulative effect and produce the minimum possible value.

$$\text{e.g.} \quad (M + 2/M) \times 100 = \left[\frac{(4.0 - 0.3)\ (1.8 - 0.1)}{(17.0 + 0.5)} \Big/ (19.7 + 0.2) \right]$$

$$\times 100 = 1.809\%$$

3. Calculation of the Per Cent ^{18}O Content

The per cent ^{18}O content was obtained by interpolation from a plot of per cent $^{18}O/O_{Ttl}$ versus per cent M + 2/M. The required plot was obtained from the following equation.

$$\text{Per cent } M + 2/M = \frac{Z\ ^{18}O}{100 - {}^{17}O - {}^{18}O} + \frac{W(W-1)}{2}\left[\frac{C}{100 - C}\right]^2 +$$

$$\frac{X(X-1)}{2}\left[\frac{H}{100 - H}\right]^2 + \frac{Z(Z-1)}{2}\left[\frac{{}^{17}O}{100 - {}^{17}O - {}^{18}O}\right]^2 + WX\left[\frac{C}{100 - C}\right]$$

$$\left[\frac{H}{100 - H}\right] + WZ\left[\frac{C}{100 - C}\right]\left[\frac{^{17}O}{100 - {}^{17}O - {}^{18}O}\right]$$

$$+ XZ\left[\frac{H}{100 - H}\right]\left[\frac{^{17}O}{100 - {}^{17}O - {}^{18}O}\right]$$

where: Z = the number of oxygens (O) in the compound

X = the number of hydrogens (H) in the compound

W = the number of carbons (C) in the compound

and the natural abundances of the isotopes are as follows:

^{18}O = 0.20 %

^{17}O = 0.039%

^{13}C = 1.069%

^{2}H = 0.016%

The equation is solved by repetitive substitution of values of per cent $^{18}O/O_{Ttl}$ ranging from 0.20 to 50.00 to obtain corresponding values of per cent M + 2/M. The plot that results is specific for that compound and is usually a curve.

In the example given, the values which result are: maximum -- 2.138%, reported ("best") -- 1.830%, and minimum -- 1.437%.

4. Calculation of the Per Cent Exchange

These values are obtained by dividing the actual per cent

excess ^{18}O incorporated in the alcohol by the theoretical maximum possible value.

The first of these values was obtained by substraction of the natural abundance of ^{18}O (0.233% for the trans-ester, 0.215% for the cis-ester) from the experimentally observed per cent ^{18}O content.

The second of these values is the total amount of ^{18}O available to the ester alkyl oxygen divided by the number of oxygen atoms involved in the equilibration, minus the natural abundance of ^{18}O in the alkyl oxygen of the ester being pyrolyzed. This value is obviously dependent on whether, in the system being studied, only the two oxygens of the ester linkage equilibrate, or whether all four oxygens of both the ester linkage and acid function equilibrate. The result of these two alternatives was calculated as follows.

i Two Oxygen Equilibration

The total amount of ^{18}O available is 11.263% for the trans-ester and 11.245% for the cis-ester, where 11.030% comes from the ester carbonyl oxygen and the remainder comes from the alkyl oxygen in each case. Therefore, the theoretical maximum values are:

$(11.263/2) - 0.233 = 5.398\%$ for the trans-alcohol

$(11.245/2) - 0.215 = 5.407\%$ for the cis-alcohol

ii Four Oxygen Equilibration

Now the total amount of ^{18}O available is 33.323% for

the trans-ester, and 33.305% for the cis-ester where, in each case, the extra 22.060% comes from the oxygens of the acid function. Therefore, the theoretical maximum values are:

(33.323/4) - 0.233 = 8.098% for the trans-alcohol

(33.305/4) - 0.215 = 8.111% for the cis-alcohol

Thus, in the example given, the per cent exchange for the "best" value would be: (1.830/5.407) x 100 = 29.86% assuming two-oxygen equilibration and (1.830/8.111) x 100 = 19.91% assuming four-oxygen equilibration.

Calculation of Rate Constants for Isotope Exchange

It was assumed that the process by which exchange occurred was a first-order process and therefore, the first-order rate equation was employed:

$$\ln E_L = - kt + \ln E_o$$

where all terms are as previously defined. This may be rearranged to the following:

$$k = - \frac{\ln (E_L/E_o)}{t}$$

Thus, the value of k for a particular isotope exchange run was obtained by substitution of the appropriate values of t and E_L/E_o, where the ratio E_L/E_o was obtained from the per cent exchange.

e.g. If 19.91% exchange occurred in 33.5 min

$$k = \frac{- \ln (0.8009)}{33.5 \times 60} = 11.05$$

APPENDIX IV

Differentiation Between the Two- and Four-Oxygen Equilibration Processes

Examination of the ^{18}O labelled hydrogen phthalate esters used for the isotope exchange studies shows that there are two possible mechanisms leading to incorporation of ^{18}O in the alkyl oxygen, that is, two- or four-oxygen equilibration (Figure 13). As previously stated, it is important to know which pathway or mechanism is being followed.

Now, since all the excess ^{18}O observed in the alcohol (after LAH reduction of the ester) must have come from the phthalate moiety, then the amount of ^{18}O left in the DHX should show an exactly corresponding and mathematically predictable decrease. The specific amount of this decrease will be determined by the mechanism by which the alcohol gained the ^{18}O; either entirely from the carbonyl (of the ester linkage) oxygen, or from all three enriched oxygens of both the ester and the carboxyl functions. Therefore, a knowledge of the exact amount of the ^{18}O gained by the alkyl oxygen allows one to predict the amount of ^{18}O left in the DHX, depending on whether two- or four-oxygen equilibration occurred. A comparison of the two predicted values with the experimentally observed value will show which

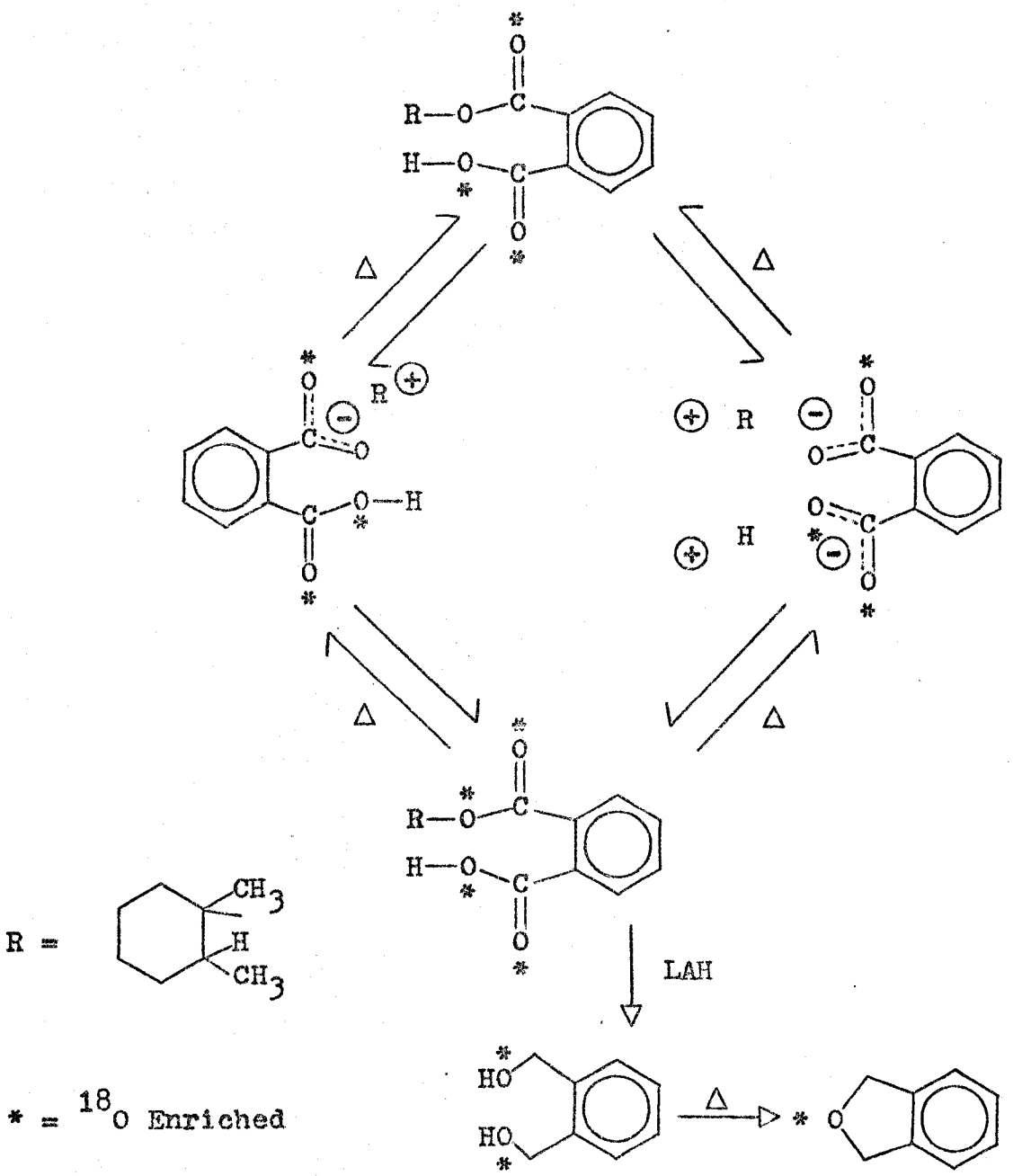

Figure 13 - Exchange Pathways in The Partial Pyrolysis of ^{18}O Labelled cis- and trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate Esters

mechanistic pathway was followed.

As in the case of the ^{18}O contents of the alcohols, maximum, reported ("best") and minimum values may be calculated both for the predicted values and the observed values. These will serve as an error range to show what extent the predicted and observed values overlap each other.

Direct mass spectral analysis of DHX or its di-trimethylsilyl derivative was not possible; therefore, the samples were analyzed as the corresponding 1,3-dihydroisobenzofuran (DHIF). Flash pyrolysis at 280° and glc separation allowed this material to be successfully analyzed at 15 ev. The results of these analyses were then compared with the predicted values which were ½ the value predicted for the DHX. An example prediction follows.

Assume:

-- each labelled oxygen atom in the hydrogen phthalate ester contains 10 atom per cent ^{18}O

-- the unlabelled alkyl oxygen contains no ^{18}O

-- after partial pyrolysis and reduction, the product cyclohexanol contains 5 atom per cent ^{18}O.

Now if all 5% came only from the ester carbonyl oxygen, then the DHX would contain:

5%	^{18}O from the ester carbonyl
10%	^{18}O from either oxygen of the carboxyl function
15%	total in the DHX or 7.5% in the DHIF

However, if the 5% came equally from all three labelled oxygens, then the ester carbonyl and each of the carboxyl

oxygens would contain an equal amount of ^{18}O -- (30-5)/3 = 8.33%. Therefore, the amount of ^{18}O left in the DHX would be:

8.33%	from the ester carbonyl
8.33%	from either oxygen of the carboxyl function
16.66%	total in the DHX or 8.33% in the DHIF.

Thus, it is apparent that no matter what the amount of ^{18}O in the alcohol, the two- and four-oxygen equilibration mechanism will predict differing amounts of ^{18}O to be left in the DHX. Therefore, a comparison of the two predicted values with the experimentally observed value should show which form of equilibration actually occurred.

It should be noted that such an analysis assumes the following:

-- that the starting atom per cent ^{18}O content of all oxygens in the starting ester is exactly known
-- that we are able to accurately measure the ^{18}O content of all products
-- that none of the work-up procedures or handling procedures will alter the ^{18}O content of either products or starting materials.

It is felt that all these prerequisites have been met.

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